

## Some Contemporary Advances in Physics—X The Atom-Model, Third Part

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### M. A VERY BRIEF RECAPITULATION OF WHAT HAS GONE BEFORE

**A**BUNDANT evidence of many kinds exists to show that each and every distinct sort of atom is especially adapted to possess energy, not in any random quantity whatsoever, but in certain peculiar, definite, characteristic amounts. An atom having energy in one of these particular amounts apparently cannot add arbitrary quantities to its store, nor yield up arbitrary quantities from it; whenever the atom receives or whenever it gives energy, it receives or gives only just so much as is exactly sufficient to raise or reduce its supply to some one among the others of these distinctive quotas. For each of the chemical elements there is a great system of these distinctive energy-values. They are determined chiefly by analyzing spectra, and for most of the elements—the exceptions being those of which the spectra are excessively complicated—many of them have been evaluated very accurately and set down in tables. The system of distinctive energy-values for any element is a very important feature of that element; perhaps, indeed, the most important feature of all.

It is customary to say that when an atom acquires or surrenders energy, it passes from one into another state; the various states corresponding to its various distinctive energy-values are called its "Stationary States." This is a name which suggests, and is doubtless meant to suggest, that the energy-value of the atom is but one among many of its features, all of which change when the energy-value changes. This is a legitimate idea; theorizing about the atom consists in speculating about just such features. But the reader will go far and grievously astray if he lets the name signify to him that many of them are directly and definitely known. In some few cases there is good reason to believe that we know the magnetic moment of an atom in its normal state. Beyond these the energy-values are all that are known. If the reader chooses everywhere to replace "Stationary State" by "energy-value" he will be holding fast to the physical reality, to the one thing not liable to be compromised by the future trends of thought.

An atom may pass from one Stationary State to another because of colliding with an electron or another atom of the same or a different

kind; or by absorbing radiation it may pass from one Stationary State to another of higher energy; or it may pass spontaneously from one Stationary State to another of lower energy. In this last case, it emits radiation of which the frequency  $\nu$  is related to the difference  $\Delta U$  between the energy-values of the initial Stationary State and the final one by the equation

$$\nu = \Delta U/h, \quad (h = 6.56 \cdot 10^{-27} \text{ erg/sec.})$$

The same equation governs the last case but one, in which it connects the frequency of the absorbed radiation with the energy-difference between the two Stationary States from and into which the atom passes. On this equation is founded the method of analyzing spectra which is the most accurate and most widely applicable method of determining the energy-values of Stationary States. The other ways in which atoms are caused to pass from one State to another lead to methods of determining these states, which are almost useless for accurate measurements, but invaluable as controls.

The energy-values of the various Stationary States of an atom are interrelated, and sometimes it is possible to express a long sequence of them by means of a simple or a not very complicated formula. There are also interrelations between the distinctive energy-values for different elements; and this statement is meant to apply also to atoms from which electrons, one or more, have been detached, which should be considered as distinct though not as stable elements. There are unmistakable numerical relations among the Stationary States which come into being when atoms are subjected to electric or to magnetic fields. Finally there is the important principle that the spontaneous transitions between various pairs of states, which result in spectrum lines, do not occur equally often; and yet the relative oftenness or seldomness of their occurrence is itself regulated by laws. One finds instances in which transitions from a state  $A$  to a state  $B_1$  are just twice as common as transitions from  $A$  to a state  $B_2$  close to  $B_1$ . One finds instances in which transitions from a state  $A$  to a state  $B$  do not occur at all under usual conditions and an atom in state  $A$  cannot get into state  $B$  without touching at some state  $C$  from which  $A$  and  $B$  are both accessible. It is possible so to arrange the Stationary States of an atom that by looking at the situations of any two states in the arrangement, one can tell immediately whether direct transitions between them do occur or do not; and this arrangement is found to be suited to, even to be demanded by the numerical interrelations to which I alluded above. Upon these facts the classi-

fications of the Stationary States are founded, and the notations by which they are named.

The atom-model to which this article is devoted, the atom-model of Rutherford and Bohr, is designed to interpret these facts of the Stationary States, but not these alone. It is designed also to interpret certain experiments—chiefly, though not altogether, experiments on the deflections suffered by minute flying charged particles when they pass through matter—which indicate that an atom consists of a positively-charged nucleus with a congeries of electrons around it. Specifically, the results of these experiments agree with the notion that the  $N$ th element of the Periodic Table consists of a nucleus with positive charge  $Ne$  and  $N$  electrons surrounding it; and this is the simplest and most satisfying notion with which they do agree. Yet there is something paradoxical about this atom-model; for electrons could neither stand still nor yet revolve permanently in orbits around a nucleus, if they conformed to the laws of electrostatics. Also there must needs be something paradoxical about any attempt to interpret the Stationary States by this model, for there is nothing inherent in it to make any energy-value preferable to any other. Under these circumstances Bohr's procedure was, resolutely to accept both paradoxes at once, and to say that the electrons can revolve permanently in those and just those particular orbits, whereby the energy of the atom assumes the particular values which are those of the observed Stationary States. This is easy to say; but it is not important, unless one succeeds in showing that those and only those particular orbits are set apart from all others by some peculiar feature, are distinguished by conforming to some particular principle, which can be exalted into a "Law of Nature" to complement or supersede the laws of electrostatics. Otherwise the atom-model would be of no value.

Thus in order to make the test of the atom-model, it is necessary to trace these orbits. One is confronted with this problem of orbit-tracing: *Given*: the observed energy-values of the Stationary States; *required*: to trace the orbits such that, when the electrons travel in them, the energy of the atom has these observed values. If this problem cannot be solved, it is impossible to take the next and essential step of ascertaining whether these particular orbits are distinguished in any particular way from all the other conceivable ones.

In the case of a single electron revolving about a nucleus, this problem is sometimes soluble. If the mass of the electron is regarded as invariable, and no outside influences are supposed to act upon the atom, then the solution is comparatively easy to attain. It was performed in the Second Part of this article. If an external magnetic

field is superposed, the problem is scarcely more difficult; if an external electric field is superposed, it is difficult but soluble—provided always that the mass of the electron be supposed invariable. If the mass of the electron is supposed to vary with its speed as the theory of relativity requires, and as certain experiments suggest, the problem remains soluble—provided that no outside influences act. For all these cases the orbits which yield the observed energy-values have been traced; and certain features have been shown to be common to all of these “permitted” orbits, and to no others, so that by these features the permitted orbits are set apart from all the rest. Inversely, anyone who is told what these features are, and who is sufficiently adept in dynamics, can trace all the orbits which display them and calculate the energy-values for these orbits and so predict the energy-values of all of the Stationary States of an atom consisting of a nucleus and a single electron. Such orbits are known as *quantized orbits*. The rules whereby they are set apart from all the multitude of orbits not permitted are the *Quantum Conditions*; which some one, it is to be hoped, will some day succeed in deriving from a general Principle of Quantization.

The most general way of phrasing these conditions is difficult to grasp, and the more intelligible ways are not the most general. The most general conditions yet formulated are not adequate for all cases; the completely adequate principle is yet to be discovered. For the purposes of this summary and of most of what follows, a very limited expression of the Quantum Conditions will be sufficient. In the Second Part of this article it was proved that the permitted orbits of an electron of invariable mass revolving in an inverse-square field such as is supposed to surround a bare nucleus, are certain ellipses. It was further stated, without proof, that if the electron of invariable mass revolves in a central field which deviates slightly from an inverse-square field, then the permitted orbits are certain “rosettes” or precessing ellipses—each orbit may be traced by imagining an ellipse revolving steadily in its own plane around the source of the central field (I will say the nucleus) at one of its foci. All the orbits are rosettes; the permitted orbits are certain rosettes which are distinguished from the others by a distinctive feature. One way of expressing this feature involves the angular momentum  $p_\phi$  and the radial momentum  $p_r$  of the electron. In terms of the mass  $m$  of the electron, its distance  $r$  from the nucleus, and its angular velocity  $d\phi/dt$  about the nucleus, these quantities are by definition:

$$p_r = m(dr/dt), \quad p_\phi = mr^2(d\phi/dt). \quad (1)$$

The "principle of quantization" is, that the permitted orbits are marked out from all others in that they fulfil these conditions, which are the Quantum Conditions:

$$\int p_r dr = kh, \quad (2)$$

$$\int p_r dr + \int p_\phi d\phi = nh. \quad (3)$$

In these equations each integral is taken around one complete cycle of the corresponding variable;  $h$  stands for Planck's constant, and  $n$  and  $k$  take the values of all positive integers,  $k$  never surpassing  $n$ .

There is an alternative way of phrasing these quantum-conditions, which is much easier to visualize; but it emphasizes what are probably accidental features of the permitted rosettes, rather than fundamental ones. The rosettes are, as I have said, precessing ellipses; the major axes  $2a$  and the minor axes  $2b$  of these ellipses are, for the permitted rosettes

$$2a = n^2 h^2 / 2\pi^2 e^2 m, \quad (4)$$

$$2b = (k/n) 2a = k n h^2 / 2\pi^2 e^2 m, \quad (5)$$

in which  $n$  and  $k$  take as before the values of all positive integers,  $k$  not surpassing  $n$ .

Exactly the same principle governs the permitted orbits of an electron revolving in a perfect inverse-square central field, but varying in mass when its speed varies, as the theory of relativity requires. In this case also the orbits are rosettes, and the permitted orbits are particular rosettes set apart from all the others in that they fulfil (2) and (3), therefore automatically (4) and (5). The energy-values of these permitted orbits agree closely with those of the observed Stationary States of hydrogen and of ionized helium, the atoms of which are the only atoms believed to consist of a nucleus and one electron. Inversely, the orbits required to interpret the observed Stationary States are set apart from all the other conceivable orbits by the features expressed by (2) and (3), and by (4) and (5). On these close numerical agreements for hydrogen and ionized helium, and on other numerical agreements for the same atoms arising when external fields are applied, the prestige of Bohr's atom-model is founded.

The integers  $n$  and  $k$ , the *total quantum number* and the *azimuthal quantum number*, are used as indices to symbolize the various Stationary States of hydrogen and ionized helium to which they correspond. Thus the symbol " $3_2$ " stands for the Stationary State of either atom,

which in the atom-model is realized when the electron circulates in a rosette, or precessing ellipse, for which  $n=3$  and  $k=2$ . Orbits for which  $k=n$  are circles; orbits for which  $k < n$  are (precessing) ellipses, and the farther  $k$  falls below  $n$  the more eccentric (narrower) is the ellipse, although its major axis is independent of  $k$ . I have repeated all of these statements about precessing ellipses and their quantum-numbers, because a great part of the speculation about atoms possessed of more than one electron consists of persevering and obstinate attempts to interpret their behavior by as nearly as possible the same ideas.

It is essential to remember also that all the energy-values of the Stationary States are reckoned from the "State of the Ionized Atom," in which State the energy—i.e., the energy of a system composed of one atom deprived of an electron, and one electron far away—is equated to zero.

#### N. INTRODUCTION TO THE SPECULATIONS ABOUT ATOMS WITH MORE THAN ONE ELECTRON

All atoms, except those of hydrogen and ionized helium, possess more than one electron. There is much evidence of various kinds for this assertion; and certainly the spectra of these other atoms cannot be interpreted as those of the first two have been. Thus we are confronted with the problem of a system composed of a nucleus and more than one electron. The similarities between the spectra of hydrogen and ionized helium, and those of other elements, are important enough to make it desirable to use the same sort of explanation. We imagine the various electrons, when there are two or more, each to describe certain permitted orbits, set apart from the multitude of other conceivable orbits by peculiar features expressible by a Principle of Quantization.

Here at the outset we meet with the great hindrance to success in this problem. It is not possible to determine what features are common to permitted orbits, for it is not possible even to trace the permitted orbits. The general problem of tracing the paths of three or more bodies, attracting or repelling one another according to the inverse-square law, remains unsolved. Considering that for centuries the related but simpler problem of celestial mechanics has been under continual and powerful attack, the general problem may fairly confidently be regarded as insoluble. There is very little hope of ever dominating it to such an extent, that the spectra of atoms with two or more electrons can be interpreted exactly by Bohr's atom-model,

or can be used as strong support to that theory. If those two spectra of hydrogen and ionized helium were unknown, it is unlikely that the atom-model would ever have been suggested; it is more than unlikely that the atom-model could ever have been regarded as satisfactory. To this day the prestige of the atom-model results almost entirely from its achievement with those two spectra.

Why then trouble with applying it to the interpretation of other spectra? Several good reasons can be given. For instance, it may be that a system of several electrons about a nucleus acts in some respects as a unit—that its motion can be considered in some ways as the motion of a rigid body, that principles of quantization can be found for the system as a whole, similar to the principles used for quantizing the smaller and yet perhaps not more consolidated system which a single electron is. Here and there in the discussion we shall find indications that this way of thinking is suitable.

Again, one is justified in arguing that if in simple cases a certain law is proved, and if in complex cases neither that nor any other law can be proved nor disproved, then we should assume that the law proved for the simple cases extends over the complex ones. Few events in this world take place under such conditions that conservation of energy can be proved to prevail during them; yet, from the fact that conservation of energy has been verified in whatever events it has been tested, we do not hesitate to infer that it prevails in all. Bohr's model having been so strongly fortified by the data for the only two atoms for which it can be completely tested, why not assume it for the others?

And finally, there is the point that many of the data of experiment are almost universally expressed in terms of the model, so that the physical literature of today is almost incomprehensible without some knowledge of it. Unfortunate as this is, it shows that the model is a valuable aid for visualizing the facts. This justifies any model; but must not be construed as evidence for it.

It will be expedient to divide the subject substantially under these following headings.

(a) *The Helium Atom.* This, as the case of an atom composed presumably of a nucleus and two electrons, comes nearest to being amenable to calculation. Certain mechanically possible orbits of the two electrons, possessing the peculiar features of the "permitted" orbits of a single electron revolving around a nucleus, have been traced and their energy-values calculated. Not one of them has given the observed energy-value of a Stationary State of the helium atom. It is the consensus of opinion that whatever the features

which distinguish the permitted orbits may be, they are not those which prevail in the hydrogen atom.

(b) *Alkali-Metal Atoms.* For these there is reason to believe that one electron is normally located far beyond all the others, and may be supposed to revolve around a "residue" consisting of all the others and the nucleus. At a great distance, the field due to this residue will be very nearly a central field such as would surround a nucleus of charge  $+e$ ,—a hydrogen nucleus; for, from a great distance, the nucleus and the electrons of the residue will seem almost to coincide in place. Nearer in, the forces due to the electrons of the residue may be supposed to compound with that due to the nucleus in such a way that a central field, not varying as the inverse square, results. Thus rosette orbits may be expected (for this reason I quoted the principle of quantization for such orbits in Section M). An enormous amount of effort has been spent in constructing central fields, such that the rosette orbits obeying the quantum-conditions (2) and (3) have nearly the energy-values which the Stationary States of these atoms are known to possess. Always, the emission of a spectrum line is supposed to result from a transition of the outermost or valence electron from one orbit to another, the electrons of the residue being scarcely or not at all affected. Such is the general explanation for the far-reaching and yet imperfect resemblance of the spectra of these metals to that of hydrogen.

(c) *Other Elements.* As one passes across the Periodic Table from left to right along any row, the spectra rapidly lose resemblance to the hydrogen spectrum. This is taken to mean that the assumption used for alkali metals—the assumption that one electron lies far beyond the others, and executes transitions while the others remain unaffected—departs progressively further from the truth. Evidence exists that simultaneous transitions of two electrons occur, and very likely yet more drastic rearrangements taking place *en bloc*.

(d) *Building of Atoms by Consecutive "Binding" of Electrons.* An atom composed, when complete, of  $Z$  electrons arranged about a nucleus bearing the charge  $+Ze$ , may have been formed originally in  $Z$  stages by the consecutive advent of  $Z$  electrons, the first annexing itself to the bare nucleus, the second joining itself to the system composed of the nucleus and the first, and so on until as many have arrived as the nucleus is able to hold. Each of these stages should be accompanied by the emission of lines belonging to a particular spectrum; the ordinary hydrogen spectrum accompanies the formation of a hydrogen atom by the step-by-step binding of an electron to a nucleus of charge  $e$ , the ionized-helium spectrum accompanies



the joining of the first electron to a nucleus of charge  $+2e$ , the neutral-helium spectrum the adhesion of the second electron to such a nucleus. Spectra corresponding to the latest four or five stages, in the formation of atoms having many electrons when completed, have been observed. To a certain extent, but not entirely, an atom with  $Z$  electrons and a nuclear charge  $Z$  resembles an atom with  $Z$  electrons and a nuclear charge  $Z+1$ . To a certain extent, therefore, each atom in the Periodic System may be regarded as resembling the last stage but one in the formation of the next following atom. This fact is important in the interpretations of the Periodic Table.

(e) *Multiplets.* We next take account of the fact that the sequences of Stationary States, mentioned in the elementary theory and description of spectra, are actually sequences of groups of Stationary States; and inquire what may be supposed to differentiate the several states of a group from one another. An elaborate formal theory is based on the assumption that all of the electrons of what I have called the "residue" of the atom revolve, if not literally as a rigid block, at least with a resultant angular momentum which itself is quantized; and that the outermost electron revolves in its own orbit around this residue, the different Stationary States of the group differing from one another in respect of the inclination of the orbit to the axis of rotation of the residue. The theory is not quite coherent with what has gone before; and for that reason the reader should try to separate its essential qualities from its accidental ones.

(f) *Magnetic Properties of Atoms.* A magnetic field should treat a system of electrons revolving around a nucleus in the same way as it treats one electron, as was said in the Second Part of this article. One would expect that in this case, if in any, the behavior of complex atoms would resemble that of the hydrogen atom; yet there is a striking and inexplicable contrast. This, like the spectrum of the helium atom, shows that either the quantum conditions governing the hydrogen atom are not universal, or the expressions hitherto found for the quantum conditions are too limited. From the responses of atoms to magnetic fields something is learned about the magnetic properties of atoms and their residues, some part of which can be tested by direct experiment; and these experiments include what are probably, all things considered, the most perplexing and fascinating ones of recent years.

(g) *Interpretation of X-ray Spectra.* X-ray spectra are analyzed as other spectra are, and each absorption and each emission of an X-ray by an atom is associated with a transition between two Stationary States; these "X-ray Stationary States" however are distin-

guished from the others, by the circumstance that every one of them involves the absence of an electron from the atom; consequently they may be described as Stationary States of an atom-residue. There is reason to believe that each distinct State involves the absence of a particular one, or of one out of a particular group, of the electrons bound to the nucleus during the earlier stages of the imagined building of the atom by successive "binding" of electrons. The speculations about X-ray spectra consist largely in attempts to correlate the individual States with absences of particular electrons.

### O. THE HELIUM ATOM

The problem of the nucleus with two electrons, the "dilemma of the helium atom" as van Vleck calls it, is one of the most tantalizing in contemporary physics. One feels confident *a priori* that the same quantum conditions as suffice so beautifully to constrain the one-electron atom to yield the hydrogen spectrum should also suffice, when applied to the orbits of two electrons, to yield the spectrum of neutral helium. Yet the various pairs of orbits conforming to these quantum conditions, which have already been traced, have been shown (with vast expenditure of intellectual labor by some of the ablest mathematical physicists of our time) to entail energy-values for the Stationary States which are hopelessly incorrect.

For instance, one might assume that when the helium atom is in its Normal State, the two electrons are revolving in a common circular orbit about the nucleus, being at each instant located at opposite ends of a diameter; and that this permitted orbit is determined by the condition that the angular momentum of each electron, or perhaps that of both together, is  $h/2\pi$ . This seems an obvious generalization of the Quantum Conditions for hydrogen; but it yields a false energy-value for the Normal State; and there is nothing more to be said. Kemble and van Vleck demonstrated that no arrangement in which the two electrons are symmetrically placed relatively to a line through the nucleus entails the proper energy-value for the normal state. This still leaves open the possibility that the two electrons are unsymmetrically placed—a possibility which to some people seems repellent enough to be excluded. Born and Heisenberg calculated the energy-values corresponding to pairs of orbits, one of which lies far beyond the other at all points, and both of which are concordant with the Quantum Conditions. These ought to have agreed with the energy-values of the Stationary States which are remote from the normal state and near the state of the ionized

atom; but they did not. This result is commonly regarded as the strongest evidence for the belief that the Quantum Conditions valid for an atom with one electron are not valid for an atom with two.

The atom-model favored by Kramers, and hence presumptively by Bohr, to represent a helium atom in its normal state, involves two electrons moving in orbits which are not coplanar nor even plane. Planes tangent to the two surfaces upon which the orbits are traced intersect each other at  $120^\circ$  along a line passing through the nucleus, and the electrons pass simultaneously across this line at opposite crossing-points. These orbits conform to the Quantum Conditions; and the resultant of the angular momenta of the two electrons, which is the angular momentum of the entire atom, is equal to  $h/2\pi$ . This atom-model likewise fails to have the right energy-value for the normal state.

#### P. INTERPRETATION OF THE OPTICAL SPECTRA OF ALKALI-METAL ATOMS

The alkali metals (lithium, sodium, potassium, rubidium and caesium) are elements of which the atoms are easily deprived of a single electron apiece; one electron of each atom is, as the phrase goes, exceptionally "loosely bound." Many facts combine to indicate this; for instance, each of these elements enters with violence into chemical combinations, and the compounds which each forms are such as to suggest that its atom yields up one electron to the atom or atoms which join with it. Again, when a salt of one of these metals is dissolved, the molecules split up and the atoms of the metal are left wandering around in the solvent minus one electron apiece, while the atoms of the other element each hold on to one captured electron. More definite yet is the direct evidence that the ionizing potentials of the alkali metals are lower than those of any other elements in the same rows of the Periodic Table, those of rubidium and caesium being altogether the smallest known. These alkali metals follow, in the Periodic Table, immediately after the five noble gases helium, neon, argon, xenon and krypton respectively. These gases are chemically all but absolutely inert, almost never entering into combinations. Their ionizing-potentials are higher than those of any other elements in their respective rows of the periodic table, and those of helium and neon are the greatest known. The atoms of each of the alkali metals are much larger than those of the preceding inert gas.

From all these facts the inference is drawn, that the atom of each inert gas consists of a nucleus and electrons, at least the outermost

ones of which are arranged in a peculiarly stable and symmetrical fashion (as for instance, in a group of eight at the corners of a cube, though this is by no means sure); while the atom of the next following alkali metal consists of just this sort of arrangement or "inert-gas shell," now to be known as the "residue" or "kernel," and of one additional electron now to be known as the "valence-electron," usually much farther away from the nucleus.

If to such an atom-model we apply the doctrine of Stationary States, we may infer that for each and every arrangement of the electrons in the residue, or (to use more general terms) for each condition of the residue, there is a whole system of Stationary States differing from one another only in that the valence-electron travels in different ones among a system of quantized orbits. These orbits we may suppose to conform to the quantum-conditions (2) and (3), at least until convincing evidence is brought to the contrary. Such in fact is the interpretation of the system of Stationary States, transitions between pairs of which are responsible for the "optical spectrum" of each alkali metal.

An electron at a very great distance from the kernel of such an atom will experience an attraction towards it, practically indistinguishable from the attraction which would be exerted by a single (hydrogen) nucleus of charge  $+e$ . One might say that the  $(Z-1)$  electrons surrounding the nucleus of charge  $+Ze$  effectively cancel a portion  $+(Z-1)e$  of the nuclear charge; or to use a more common word, that they "screen" it. As the imagined distant electron moves inward towards the kernel, the screening will cease to be perfect. An effect should occur analogous to the "stray field" which penetrates the meshes of a grid; since the electrons of the kernel do not form a continuous shell of electricity enclosing the nucleus, the latter should make itself felt through the interstices, although this effect may be diminished by the swift motion of the electrons. All this is speculation of the wildest kind. The only deduction reasonably safe is this, that very far outside the kernel the field will be very nearly the inverse-square field due to a hydrogen nucleus of charge  $+e$ ; very near to the kernel the field will be quite incalculable<sup>1</sup>; while in between the very-far-out and the very-near-in region, there will be an intermediate region, in which there may be some chance of finding an adequately approximate expression for the field. On the existence of such a region, in which such an approximation is good enough to be valuable,

<sup>1</sup> Unless it is violently simplified by some agency or restriction of which at present we know nothing.

rests all the present hope of achieving numerically valid theories in this division of atomic physics.

One agreement between this theory and certain data may be demonstrated without making any specific approximation. The farther away the valence-electron remains from the kernel, the more nearly identical with the field of a hydrogen nucleus is the field in which it revolves, the more nearly should it behave like the electron of a hydrogen atom. Consider for instance, in a hydrogen atom, the orbit which yields the Stationary State for which  $n$  the total quantum-number and  $k$  the azimuthal quantum-number are both equal to 5. This orbit is a circle of which the radius is  $10^{-7}$  cm.; far larger than the radius of any inert-gas atom, presumably *a fortiori* far larger than the kernel of any alkali-metal atom. Were the valence-electron of such an atom to describe this circle, it would pass everywhere in a field very nearly like that of a hydrogen nucleus, and should very nearly conform to the quantum conditions for this field. It follows that an orbit drawn in the actual field, obeying the quantum-conditions  $n=5$  and  $k=5$ , would be very nearly such a circle with very nearly the same energy-value. The inference is drawn that for high values of  $n$  and  $k$ , the Stationary States of an alkali-metal atom should be very nearly identical with those of hydrogen. These orbits which lie far out from the kernel of the alkali metal atom, or from the nucleus of the hydrogen atom, have small energy-values. It may therefore be said that if we tabulate the Stationary States of the two atoms in order of decreasing energy-value, then the farther along the two tabulations we go, the more nearly should the two systems of Stationary States coincide.

This is found to be true, under a limitation. The limitation is an important aid in interpreting the arrangement of the Stationary States. It will be recalled from the First Part of this article that the Stationary States of the sodium atom are arranged in several sequences (there illustrated as columns in Fig. 7) known as the *s*-sequence and the *p*-sequence and the *d*-sequence and the *f*-sequence and others; and to these sequences successive values 1,2,3,4 . . . of a symbol  $k$  were appended. One basis for this classification is that when it is made, the occurrence or non-occurrence of transitions between any pair of Stationary States, under normal conditions, can be determined by applying the "selection-rule" that only such transitions occur as involve a change of one unit in  $k$ . Now there are two reasons for supposing that the only transitions which can occur are those in which the Azimuthal Quantum-number of the valence-electron changes by one unit. Unfortunately it is not possible to introduce these two

reasons with all the necessary background without too long a stoppage of the main current of this argument.<sup>2</sup> I must therefore set it down as an assertion, that the selection-rule is deducible from the assumption that the value of  $k$  is the Azimuthal Quantum-number of the valence-electron; which thus is 1 for all the Stationary States of the  $s$ -sequence, 2 for each State belonging to the  $p$ -sequence, 3 for the  $d$ -sequence, and 4 for the  $f$ -sequence. The feature common to the various Stationary States of a sequence is, therefore, the Azimuthal Quantum-number of the valence-electron—if this atom-model is valid.

This being assured, the conclusion is drawn that, since  $k$  is higher for the  $f$ -terms than for the  $d$ -terms, higher for the  $d$ -terms than for the  $p$ -terms and higher for the  $p$ -terms than for the  $s$ -terms; since, therefore, the  $f$ -orbits are *ceteris paribus* more nearly circular than the  $d$ -orbits and less inclined to stretch down into the neighborhood of the kernel, the  $d$ -orbits more nearly circular than the  $p$ -orbits and the  $p$ -orbits more nearly circular than the  $s$ -orbits—therefore the approximation of the sodium terms to the hydrogen terms will be most nearly perfect for the  $f$  (and higher) sequences, less so for the  $d$ , less for the  $p$  and worst for the  $s$ -terms. This also is verified. It reinforces the opinion that the  $k$ -values assigned to the various sequences are actually their azimuthal quantum-numbers.

As the different States of a single sequence share a common Azimuthal Quantum-number, they must differ—supposing always that this atom-model is valid—in their Total Quantum-number. Consecutive States of a sequence presumably have consecutive values of the Total Quantum-number (although sometimes one meets with a break or a jolt in the continuity of a sequence, suggesting a departure from this rule). The meanings of the Total Quantum-number  $n$  and of the Azimuthal Quantum-number  $k$  for elliptical orbits are such, that  $n$  can never be less than  $k$ . Hence the value of  $n$  for the first Stationary State of the  $s$ -sequence may be unity, or greater; but the values of  $n$  for the first terms of the  $p$ -sequence, the  $d$ -sequence and the  $f$ -sequence may not be less than 2, 3, and 4, respectively.

Strange as it may seem, there is no perfectly satisfactory way of determining the value of  $n$  for all Stationary States. Generally it happens that the various States of an  $f$ -sequence, that of sodium for example, agree so closely with those States of hydrogen which form an  $n_4$  sequence, that there is little hesitation in attaching to each of the  $f$ -States the same value of  $n$  as is borne by that State of the hydrogen atom which coincides with it so nearly. For instance,

<sup>2</sup> These being (*verbum sapienti*) the argument associated with the name of Rubino-wicz, and the argument deduced from the Principle of Correspondence.

the first *f*-State of sodium has very nearly the same energy-value as the  $4_1$  State of hydrogen; the second *f*-State of sodium nearly coincides with the  $5_1$  State of hydrogen, and so forth along the sequence. Hence to the successive States of the *f*-sequence of the sodium atom one attaches with confidence the symbols  $4_1$ ,  $5_1$ ,  $6_1$ , and so onward. In some cases this is practicable for the terms of the *d*-sequence also; but never for those of the *s*-sequence. The Stationary States of the *s*-sequence depart so far from those of hydrogen, that one cannot with any security conclude what values of the Total Quantum Number should be assigned to them. It used to be assumed that  $n=1$  for the first term of the *s*-sequence and  $n=2$  for the first term of the *p*-sequence, and the usual notation for the Stationary States reflects this supposition; which however is neither necessary nor probable.

All of the foregoing interpretations are based upon a theory of the alkali-metal atoms which may be summarized in this way: as the hydrogen atom is supposed to consist of a nucleus surrounded by an inverse-square field through which an electron travels always in one or another of certain orbits determined by quantum-conditions, so also the alkali-metal atom is supposed to consist of a kernel surrounded by a not-inverse-square field through which an electron travels always in one or another of certain orbits determined by identical quantum-conditions. As the Stationary States of the hydrogen atom correspond each to a certain orbit and are designated each by certain values of two quantities  $n$  and  $k$ , or for short by a symbol  $n_k$  indicating the features of that orbit, so also the Stationary States of the alkali-metal atom correspond each to a certain orbit and are designated each by a symbol  $n_k$ . For the hydrogen atom we recognize the proper  $n_k$  for each Stationary State because of the wonderful numerical agreement between Bohr's theory and the experimental values for the energy of each State. For the alkali-metal atom we can only guess the proper  $n_k$  for each Stationary States from indications of much lesser evidential value. We suppose, however, that  $k=1,2,3,4$  for the various States of the *s*, *p*, *d* and *f* sequences, respectively; so that the *s*-sequence is like the  $n_1$  sequence of hydrogen, the *p*-sequence like the  $n_2$  sequence, and so on. Of the values of  $n$  we are moderately sure for the *f* and *d* sequences, quite uncertain for the terms of the *s* and *p* sequences.

One may now wonder whether it is possible to invent a central field, such that the orbits traced in it according to the quantum-conditions (2) and (3) would yield a series of energy-values agreeing with the observed energy-values of the Stationary States of (let me

say) the sodium atom. It takes a certain amount of faith to go about the business of designing such a central field; for the model imagined for the sodium atom involves ten electrons around the nucleus in addition to the one "valence" electron for the benefit of which the field is being devised; and one might expect these ten electrons to be rushing around the nucleus in uncoordinated and non-recurring paths, never at any two instants similarly placed and similarly moving, never at any two instants exerting the same influence upon the valence-electron. Yet the Stationary States of the sodium atom are as sharply defined as those of the hydrogen atom; and this may be thought to mean that the ten electrons of the kernel are constrained to a unity and a fixed relationship, like that of the members of a machine if not like that of the parts of a rigid body, which translates itself into an influence upon the valence-electron not unlike that of a central field.

At all events, several physicists working independently in various nations have taken the not inconsiderable trouble of devising central fields to fulfil the condition required; and they appear to have achieved a respectable success. It is not easy to decide what this success requires the rest of us to believe; perhaps it is formally possible to devise a central field to account for *any* set of Stationary States; I am not sure whether this question has been adequately examined. Some have felt confident enough to say that the results show which of the Stationary States correspond to orbits of the valence-electron which "penetrate into the kernel" and which to orbits that remain in all their circuit quite outside of the kernel. It is to be hoped that this problem will become clearer in the next few years. At this point I will add only, that the orbits traced for the valence-electron are rosette orbits in which the precession is very rapid, so that consecutive loops of a rosette are inclined at a considerable angle to one another. In the model for the hydrogen atom, the consecutive loops of a rosette orbit lie so close together as to be indistinguishable when drawn to scale on an ordinary sheet of paper (the separation between them was much exaggerated in Fig. 3 of the Second Part of this article). In these atom-models, the orbit looks rather as if it were drawn along the edges of the blades of an electric fan.

#### Q. INTERPRETATION OF THE OPTICAL SPECTRA OF OTHER ELEMENTS

As soon as we step from the first column of the Periodic Table into the second, the obstacles to such a theory as we have hitherto tried to hold are gravely increased. There is evidence of several kinds



which seems to bear upon the arrangement of the electrons in the atoms; but some of it leads to conclusions opposite to those which the remainder suggests.

On the one hand, line-series are discernible in the spectra of elements in the second and the third columns of the Table, and even in those of some others; and from these line-series, systems of Stationary States are deduced which resemble those ascertained for the alkali-metal atoms; and it is natural to extend the same explanation from that case to these, supposing again that each atom consists of a nucleus and a certain number of electrons, all but one of which are tightly bound into a residue, around which the one remaining electron circulates in one or another of various quantized orbits.

On the other hand, the chemical behavior of these elements does not confirm this easy classification of the  $N$  electrons of an atom into  $(N-1)$  very-tightly-bound electrons and one which is very loosely bound. Thus, the atoms of elements of the second and third columns of the Periodic Table—"alkaline-earth metals" and "earth metals," as they are called—when floating in water as the fragments of molecules of dissolved salts of these elements, are found to be deprived of two and of three electrons, respectively; and the composition of these salts is such as to suggest that the atoms of the other element or elements involved in them have annexed two or three electrons, respectively, from the alkaline-earth atom or from the earth-metal atom. These facts suggest rather that the  $N$  electrons of an alkaline-earth atom, or of an earth-metal atom, should be classified into  $(N-2)$  or  $(N-3)$  very-tightly-bound electrons and two or three which are loosely-bound, respectively. The very tightly bound electrons will be equal in number to, and presumably arranged like, the electrons of the atom of the next preceding inert gas. Henceforth I will reserve the word "kernel" for such a system, and the word "residue" for what is left behind when one electron is separated in fact or in imagination from the atom. Thus these two words will not mean the same thing except in special cases, such as those of the alkali-metal atoms.

Specifically, let us consider the four consecutive elements argon (inert gas, 18th element of the Periodic Table), potassium (alkali metal, 19th element), calcium (alkaline-earth metal, 20th element), and scandium (earth-metal, 21st element).

The evidence from chemistry and from electrolysis impels us to think that the argon atom consists of a nucleus surrounded by (eighteen) electrons tightly bound, in a stable and imperturbable arrangement; that the potassium atom consists of a kernel much like the argon atom, with one additional electron loosely bound and hence

generally far beyond; that the calcium atom consists of the same sort of kernel and two loosely-bound electrons, the scandium atom of the same sort of kernel and three outer electrons.

The Stationary States of the potassium atom have been interpreted as corresponding to various quantized orbits which a single outer electron describes around an unchanging residue; the lines of its spectrum have been attributed to leaps of this electron from one orbit to another, the residue remaining unaltered. There is nothing incompatible between this and the previous conception of the potassium atom.

The Stationary States of the calcium atom resemble, in their arrangement, those of the potassium atom sufficiently to make the same general sort of an explanation desirable,—to make it desirable to suppose that one electron is loosely-bound and remote from the nucleus, the other nineteen tightly-bound and near the nucleus; one loosely-held electron versus nineteen tightly-held ones. But the evidence from chemistry and electrolysis demands two loosely-held electrons versus eighteen tightly-held ones.

One might try to evade the dilemma by supposing that the calcium atom is a sort of three-stage construction, with eighteen electrons congregated in a kernel around the nucleus, a nineteenth far out by comparison with the nucleus, a twentieth far out by comparison with the nineteenth. For interpreting spectra, the residue of the atom would be the kernel or "inert-gas shell" and the nineteenth electron, the valence-electron would be the twentieth. For interpreting chemical data, the residue of the atom would be the inert-gas shell. This conception would rescue the interpretation of the calcium spectrum made after the fashion of the one just expounded for alkali-metal atoms. It would probably demand a larger atom, or a more shrunken kernel, than other data will allow.

Or one might suppose that the nineteenth and the twentieth electron are on the whole about equally remote from the nucleus, and yet it is possible for one of them to change over between any two of a vast system of quantized orbits without greatly affecting the other. There is certain evidence for this conception which I shall presently narrate.

Or one might suppose that the nineteenth and the twentieth electron are a system by themselves, and that each Stationary State corresponds to a particular configuration of this system, so that each line of the spectrum is attributed to a leap not of either electron separately but of both together. This idea seems to be gaining ground rapidly in dealing with atoms composed of a kernel and several outer electrons,

three or four or five or six or seven. The preceding notion might be brought under it as an especial case. If it is accepted the theory of atoms other than the alkali-metal atoms will inevitably be more complex than the theory mentioned for these in section P.

An interesting feature of some of these spectra discloses that the residue of the atom may exist in either of two distinct states. It will be recalled that the energy-values of the Stationary States have been measured from the state of the ionized atom, to which the energy-value zero is assigned. In this fundamental state, one electron and the residue of the atom are completely sundered; and the energy-value of any other Stationary State is the energy required to tear the electron completely out of the atom when the latter is initially in that Stationary State. This definition implies that the state attained when the electron is completely separated from the rest of the atom is determinate and unique. Such must be the case if the atom consists of an invariable nucleus and one electron, as in hydrogen; but if the atom contains several electrons, there is no *a priori* reason for excluding the possibility that there may be several "states of the ionized atom"; in each of these states one electron will be far away, but the residue will have as many different arrangements as there are different states. Extending this idea, one infers that there may be two or more distinct sets of Stationary States for certain elements, each set culminating in a different final configuration of the residue,—that is to say, of the ionized atom.

Several instances of atoms possessing two such distinct families of Stationary States are known; the most noted is probably that of neon, but I will describe the case of calcium, lately interpreted by Russell and Saunders and independently by Wentzel. Two families of terms "primed" and "unprimed," had been identified in the spectrum of this element, and important sequences of each could be followed sufficiently far to make the extrapolation to the limit not too daring. The limits were different, showing that the amount of energy required to separate an electron from an atom initially in its normal state had two values differing from one another by 1.72 equivalent volts. Consequently the residue may remain (it is not necessary to assume that it can long remain) in either of two States differing from one another (when the extra electron is far away) by this amount.

At this point a very significant numerical agreement enters upon the scene. The residue of the calcium atom, the *ionized-calcium* atom, has itself a spectrum which is known, and from which its system of Stationary States has been learned and mapped. Like the systems of Stationary States possessed by neutral atoms, this one includes

$s$ ,  $p$ ,  $d$  and other sequences. The Normal State of the ionized-calcium atom belongs to the  $s$ -sequence; following the usual custom it may be called the  $(1, s)$  State. The State of next lowest energy-value, the "next-to-normal" State (so to speak) belongs to the  $d$ -sequence, and may be called the  $(3, d)$  State. The energy-difference between the  $(1, s)$  State and the  $(3, d)$  State is 1.69 volts. This agrees within the error of the experiments with that value 1.72 equivalent volts, which was found for the energy-difference between the two conditions, in either of which the residue of the calcium atom might be left after the twentieth electron is abstracted. This agreement shows that the extraction of the 20th electron from a calcium atom may leave the residue either in the  $(1, s)$  State or in the  $(3, d)$  State.

If now we remember that the ionized-calcium atom is comparable with the potassium atom (and with alkali-metal atoms generally) having as it does eighteen electrons very tightly bound as a kernel around the nucleus and one electron loosely held—then it is reasonable to use the same interpretation of its Stationary States as was expounded in Section P; and to suppose that when the ionized-calcium atom is in the  $(1, s)$  State that loosely-held electron is revolving in a certain  $n_1$  orbit, and when the atom is in the  $(3, d)$  State the electron is revolving in a certain  $n_3$  orbit. Thus the extraction of the 20th electron of the calcium atom may be supposed to leave the 19th electron sometimes in the one, sometimes in the other of these two orbits.

We may now inquire whether the 19th electron will always remain in its  $n_1$  orbit, or in its  $n_3$  orbit as the case may be, when the 20th electron reenters the atom, descending from one orbit to another. Here it is necessary to watch one's mental steps very closely; for one is liable to slip into the naive notion of a particular orbit, say for instance a  $3d$  orbit, as a fixed and permanent railway-track around which the electron continually runs until something violent derails it. This could not be true unless (to take this special case) the 20th electron had no influence whatever upon the 19th. Were it so, every Stationary State of the one family would differ by the same amount, 1.69 equivalent volts, from the corresponding State of the other family. In fact, the energy-difference between corresponding States varies from one pair to another. This may well be simply because the approach of the 20th electron so alters the forces acting upon the 19th, that its orbit is changed both in geometry and in energy-value, while remaining still identified with the same values of its quantum-numbers. The experiments neither prove nor disprove this; it is commonly accepted as true.

It is a very important fact that the atom may pass from a State of one family to a State of the other,—in terms of the model, that the 19th electron passes from its  $n_3$  orbit to its  $n_1$  orbit, and simultaneously the 20th electron makes some transition or other of its own. The emitted radiation contains the energy resulting from both changes simultaneously, fused together without any discrimination.

#### R. BUILDING-UP OF ATOMS BY "BINDING" OF SUCCESSIVE ELECTRONS

I next point out that the processes whereby the lines of an optical spectrum are emitted may be regarded, if this theory of the atom is valid, as stages in the gradual formation of an atom. Consider the hydrogen spectrum to begin with; each line is emitted as the atom passes from one Stationary State to another of lower energy-value, the state of least energy being the Normal State of the perfected atom and the state of greatest energy being the condition in which the atom-residue and its electron are torn apart. The various lines of the spectrum correspond to various partial steps along the path from the latter of these states to the former, to various stages of the formation of a hydrogen atom from two separated parts. The specific conception of each Stationary State as a definite orbit of the electron about a nucleus merely reinforces this way of envisaging the process. In the spectra of ionized helium and of neutral helium, we read the testimony of the gradual formation of a helium atom out of a nucleus and two electrons initially quite dissevered. The various lines of the ionized-helium spectrum correspond to different stages in the advance of an electron from the state of freedom to the state of most stable association with a nucleus of charge  $2e$ , or in Bohr's language, to different stages in the "binding" of an electron by a nucleus of charge  $2e$ . The various lines of the neutral-helium spectrum correspond to stages in the "binding" of a second electron by a system composed of a nucleus of charge  $+2e$  and an electron already bound to it. Thus the two spectra of helium testify to two consecutive processes in the upbuilding of a helium atom out of its constituent parts.

The process of building up an atom, by successive adhesions of electrons to an incomplete electron-system surrounding a nucleus—that is to say, the process of building a system of  $Z$  electrons around a nucleus bearing the charge  $Ze$ , out of a system of  $(Z-b)$  electrons surrounding the nucleus, by consecutively adding  $b$  electrons one after the other—evidently occurs very profusely in intense high-current high-voltage discharges in vapours, such as the condensed

spark and above all Millikan's "Vacuum Spark." To take instances from the work of Millikan and Bowen, Paschen, and Fowler: in the spectra of such discharges lines have been identified which belong to atoms for which  $Z=14$  and  $b$  has the several values 1,2,3,4 (four stages in the building of a silicon atom); and to atoms for which  $Z=10+b$  and  $b$  has the several values 1,2,3,4,5,6. Many of these spectra of multiply-ionized atoms have not yet been analyzed, but the work is proceeding rapidly. There is reason to hope that within a few years we shall be in possession of interpreted spectra not only of many systems of  $Z$  electrons about a nucleus of charge  $Ze$ , but also of many systems of fewer than  $Z$  electrons about nuclei of charge  $+Ze$ . This may be highly important, as I will try to show by an illustration. We will consider two consecutive elements of the periodic table; sodium ( $Z=11$ ) and magnesium ( $Z=12$ ).

A Mg atom is imagined as 12 electrons around a nucleus of charge  $+12e$ . It is formed when one electron joins itself to a Mg $+$ ion, which is composed of 11 electrons about a nucleus of charge  $+12e$ . For this process a spectrum is emitted, the so-called arc spectrum of Mg or "MgI" spectrum, which is known and analyzed. It shows that the normal state of the Mg atom is an  $s$ -state (probably of total quantum-number 3). It is likewise a singlet-and-triplet-spectrum. The first of these facts is taken to mean that the valence-electron, or *twelfth electron* (the reader will see the reason for this usage, the electron in question being the last annexed out of the twelve) of the Mg atom moves in a  $3_1$  orbit. The second is taken to mean something or other about the residue of the atom, as will be shown in section S.

This residue of the atom is itself formed when one electron joins itself to a Mg $+$ ion, which is a group of 10 electrons about a nucleus of charge  $+12e$ . In this process the so-called spark-spectrum of Mg, or "MgII" spectrum, is emitted. It is known and analyzed. It shows that the normal state of the Mg $+$ ion is an  $s$ -state (probably of total quantum-number 3). It is a doublet spectrum. The first of these facts is taken to mean that the valence-electron or *eleventh electron* of the Mg $+$ ion, moves in a  $3_1$  orbit. The second is taken to mean something or other about the residue of the Mg $++$ ion.

A very interesting question now arises: is the Mg $+$ ion actually the same as the residue of the Mg atom? In other words: when a 12th electron is added to the group of 11 electrons about a nucleus of charge  $+12e$ , is the group of eleven left unchanged? If so, we have knowledge about this group from two sources. The character of the MgI spectrum (the fact that it is a singlet-and-triplet spectrum) teaches something about the group, though what it is is far from

clear. The character of the MgII spectrum teaches something about the group, viz., that its eleventh electron moves in a  $3_1$  orbit. If these two groups are just the same, then the two independently acquired facts about them may be united into a precious correlation. As a matter of fact it is generally assumed that they are nearly if not quite the same. A valuable piece of evidence bearing upon precisely this point, although relating to a different element, was described in the foregoing section.

This suggests that it would be a most desirable achievement to produce the spectra due to groups of  $(Z-b)$  electrons congregated about a nucleus of charge  $+Ze$ , for some value of  $Z$  (the higher the better) and all values of  $b$  from 0 to  $(Z-1)$ . Were this done we could almost lay claim to having witnessed the creation of an atom from fundamental particles common to all matter. We could not quite make this claim, since the nucleus of charge  $+Ze$  would still remain characteristic of that one kind of atom alone; but we should have made a substantial approach to it. However, there is no immediate prospect of achieving this except for the cases  $Z=1$  and  $Z=2$  which have already been considered. Our inability to produce the spectrum expected for  $Li++$  (i.e. for  $Z=3$  and  $b=2$ ) acts as a barrier against utterly tearing down the electron-structures of higher atoms so that they can rebuild themselves before our eyes from the foundations.

The next important question may be introduced in this fashion. Suppose that nothing were known about the spectrum called MgII, therefore nothing about the process of adding an eleventh electron to a group of ten around a nucleus of charge  $12e$ . Knowledge would still be available about the process of adding an eleventh electron to a group of ten about a nucleus of charge  $11e$ ; for this is precisely the process which creates the neutral sodium atom out of the  $Na+$  ion, and results in the emission of the NaI spectrum or arc spectrum of sodium. This spectrum is a doublet spectrum, and it shows that the normal state of the sodium atom is an  $s$ -state, probably of total quantum number 3. This last fact is taken to mean that the eleventh electron in a group of eleven electrons about a nucleus of charge  $+11e$ , is revolving in a  $3_1$  orbit. Could we have assumed that therefore the eleventh electron, in a group of eleven electrons about a nucleus of charge  $+12e$ , is revolving in a  $3_1$  orbit? There is no *a priori* certainty of this: but the observations on the MgII spectrum, as we have seen, confirm it (and also that the residue of the  $Mg+$  ion is like the residue of the Na atom, in causing the next added electron to produce a spectrum of the doublet type).

Were this generally true we could say that each atom in the periodic table is like the residue of the next atom following it; and that the  $m$ th electron in the  $n$ th atom is revolving in the same sort of orbit as the outermost electron of the  $m$ th atom, for every value of  $n$  and for every value of  $m$  less than that value of  $n$ .

However, it is not always true. To take another specific instance, consider the two elements potassium ( $Z=19$ ) and calcium ( $Z=20$ ). The spectrum KI, which is due to a nineteenth electron joining a group of 18 about a nucleus of charge  $+19e$ , and the spectrum CaII, which is due to a nineteenth electron joining a group of 18 about a nucleus of charge  $+20e$ , are dissimilar. The dissimilarity is not quite so great as to affect the normal states of the two systems, K and  $\text{Ca}^+$ , composed of nuclei of charge  $19e$  and  $20e$  each surrounded by 19 electrons; both have as normal state an  $s$ -state, apparently of total quantum-number 4; it is inferred that in each, the 19th electron revolves in a  $n_1$  orbit. If we consider, however, the first of the  $d$ -states (to which the total quantum-number 3 is commonly assigned), we see that in the KI spectrum it has a much larger energy-value than the Normal State, while in the CaII spectrum it has nearly the same energy-value. A short leap of the imagination leads to the conclusion that if we could examine the spectrum produced by a 19th electron joining a group of 18 about a nucleus of charge  $+21e$ , the  $d$ -state in question would have a smaller energy-value than any  $s$ -state. In this case it would be the Normal State itself,<sup>3</sup> and we should say that the 19th electron, in a group of 19 surrounding a nucleus of charge  $Ze$ , revolves in a  $n_1$  orbit if  $Z=19$  or  $20$ , but in a  $n_3$  orbit if  $Z=21$ .

This system of 19 electrons around a nucleus of charge  $21e$  is a doubly-ionized scandium atom,  $\text{Sc}^{++}$ . Its spectrum has not been produced, so that the foregoing sentences are still somewhat speculative. What gives them value is the inference that scandium marks a sort of a breach in the regularity of the Periodic System. For most of the elements in the Periodic System, it can be said that the atom consists of a residue which is like the atom of the preceding element, and an additional electron; and that in its turn this atom resembles the residue of the atom of the element next following. To this the regular periodicity of the properties of the elements is ascribed. But when we reach an element of which the atom has a residue distinctly different from the atom of the foregoing element, then the regular variation of the physical and chemical properties is interrupted. Scandium, as a matter of fact, is the first of a group of

<sup>3</sup> In the First Part of this article the impression may have been left that the Normal State of every atom is an  $s$ -state. This is not true; in some known cases the Normal State is a  $p$ -state, in others an  $f$ -state.



elements, the intrusion of which into the Periodic Table brings about a disruption of the simplicity of its first three rows. There are other such intrusive groups of elements, notably the celebrated groups of the rare earths. It is supposed that wherever such a group commences, there the residue begins to vary from one atom to the next. The spectroscopic evidence is lacking; it is awaited with extreme interest.

The reader will very probably have seen one or more tables of the distribution of electrons in atoms; tables in which it is stated, for instance, that the atom of sodium contains two electrons moving in  $1_1$  orbits, four in  $2_1$  orbits, four in  $2_2$  orbits, and one in a  $3_1$  orbit; or more succinctly that it contains "two  $1_1$ , four  $2_1$ , four  $2_2$  and one  $3_1$  electron." Such tables are built by piecing together bits of evidence, some of which are such as I have described in this section, while others are inferences from X-ray spectra, magnetic properties, or observations of still other kinds. That they are still highly speculative is confirmed by the fact that they are continually being remodeled. If we could produce the spectra corresponding to all the stages of formation of an atom, we should be able to set up a tabulation more reliable than any yet put together. Even then, however, we should be confronted with the question whether the addition of a new electron to a kernel fundamentally alters the distribution of those already there.

Having considered the facts at such length in this section, we are entitled to consider the theory. In the coupled cases of hydrogen and ionized helium it was shown by experiment, and rendered plausible by theory, that the Stationary States of the element with one electron and a double charge on its nucleus correspond exactly to those of the element with one electron and a single charge on its nucleus, and are endowed with fourfold the energy of these latter. This conclusion can be extended to cover the case of a valence-electron circulating in an orbit at a great distance from a kernel composed of  $(Z-b)$  electrons and a nucleus bearing the charge  $+Ze$ . The field due to the kernel will at great distances approximate the field due to a solitary nucleus bearing the charge  $be$ . We have seen already that when  $b=1$  (so that the total charge on the nucleus balances the total charge of the electrons, valence-electron included) the Stationary States corresponding to orbits for which  $n$  and  $k$  are large coincide with Stationary States of hydrogen. It follows equally that when  $b=2$ , the Stationary States for which  $n$  and  $k$  are large have approximately fourfold the energy of stationary states of hydrogen, and coincide approximately with Stationary States of ionized helium. This is verified by experiment, and so are the corresponding conclusions for the cases  $b=3$  and  $b=4$ .

## S. INTERPRETATION OF MULTIPLETS

Heretofore in the Third Part of this article I have repeated the procedure adopted in the First Part, simplifying the actual facts by writing as though the Stationary States of each atom were arranged in sequences of individual terms, each sequence being distinguished by a particular value of the Azimuthal Quantum Number. Here as there, it finally becomes necessary to concede the complexity of the facts, and recognize that the sequences in question are sequences not of individual terms, but of groups of terms. Thus for instance the sodium atom possesses a  $p$ -sequence, not of individual terms but of pairs of terms—a pair  $2p_1$  and  $2p_2$ , then a pair  $3p_1$  and  $3p_2$ , then a multitude of other pairs. For another instance, the mercury atom exhibits a  $p$ -sequence not of individual terms but of triads of terms—a triad  $2p_1$  and  $2p_2$  and  $2p_3$ , then a triad  $3p_1$  and  $3p_2$  and  $3p_3$ , and then a procession of other triads. These sequences are collected into systems: an  $s$ -sequence and a  $p$ -sequence and a  $d$ -sequence and several more constitute a system. There are singlet systems and doublet systems and triplet systems and systems of still higher *multiplicity*; and each kind of system is distinguished by a certain manner of grouping of the terms which form its various sequences. Noteworthy and peculiar laws govern these groupings; in a doublet system, for instance, the  $s$ -sequence consists of individual terms, but all the others consist of pairs of terms; in a quartet system, the  $s$ -sequence is made up of single terms, the  $p$ -sequence of triads of terms, the remaining sequences of groups of four terms each. From the First Part of this article I reprint a Table showing how the terms are grouped in systems of all multiplicities from the singlet to the octet. The numbers opposite the name of each system and under the letters of the various sequences show how many terms belong to each group in the various sequences of that system.

TABLE I

Name of System	$s$	$p$	$d$	$f$	$f'$	$f''$
Singlet.....	1	1	1	1	1	1
Doublet.....	1	2	2	2	2	2
Triplet.....	1	3	3	3	3	3
Quartet.....	1	3	4	4	4	4
Quintet.....	1	3	5	5	5	5
Sextet.....	1	3	5	6	6	6
Septet.....	1	3	5	7	7	7
Octet.....	1	3	5	7	8	8

Each atom possesses one or more such systems of Stationary States; and the particular types which an element displays depend in a definite and fairly clear manner upon the position of the element in the Periodic Table, being in fact one of the most distinctive of the periodically-varying qualities. Each atom with an even number of electrons exhibits systems which are all of odd multiplicity, and each atom with an odd number of electrons exhibits systems which are all of even multiplicity; thus magnesium, with twelve electrons, has a singlet system and a triplet system, while sodium and once-ionized magnesium, each with eleven electrons, have each a doublet system, and neon with ten has a singlet, a quintet and two triplet systems.<sup>4</sup> Remembering what was said about the consecutive binding of electrons, it will be noticed that these facts show a regular difference between the binding of the  $N$ th electron when  $N$  is odd and the binding of the  $N$ th electron when  $N$  is even. Otherwise expressed, they show that a kernel of  $N$  electrons treats an oncoming member in one or another of two distinctive ways, according as  $N$  is even or odd. The influence of magnetic fields on spectra likewise shows that this complexity of the Stationary States is a quality not negligible, but primary.

The features of the atom-model hitherto described must be supplemented with some new one if it is to cope with such facts as these. We have represented (for example) the sodium atom in its  $2p$  state by a "valence-electron" cruising with angular momentum  $2(h/2\pi)$  in an orbit around a "kernel" composed of ten electrons and a nucleus. But there are two such states instead of one; if the angular momentum of the valence-electron is to be equal to  $2(h/2\pi)$  for each of these, some other not yet mentioned feature of the atom must discriminate the two. One might, of course, again proceed as we did in discussing the "primed terms," by assuming that the kernel of the atom is in one condition when the atom is in the  $2p_1$  state, and in another slightly different condition when the atom is in the  $2p_2$  state. This would probably entail as many different conditions of the kernel as there are pairs of terms in the sodium spectrum—a great number, and yet small in comparison with the multitude which would be required by other atoms; yet such may be the eventual theory. However, it is possible to construct for these facts an atom-model out of two revolving parts, whereby different Stationary States of a group are represented not by varying the condition of either part separately,

<sup>4</sup> Hydrogen and ionized helium are not included under this rule. Helium shows a singlet and a doublet system together, a combination which violates the rule as stated, unless the doublet system is really a triplet system in which two states of each triad are too close together to be distinguished.

but by varying the relative orientation of the two. Although this theory has not been harmonized with those which I have hitherto recited, it is competent in its own field; and for that reason I present it.

We will imagine that the atom is represented by a combination of two flywheels, two whirling objects, endowed each with angular momentum. These angular momenta are vectors, pointing along the directions of the axes of rotation of the respective flywheels, and having certain magnitudes. I will designate them temporarily as  $P_V$  and  $P_R$ , each symbol standing for a vector generally and also (when in an equation) for its magnitude. The angular momentum of the entire atom, which is necessarily constant in magnitude and in direction so long as the atom is left to itself, is the resultant of  $P_V$  and  $P_R$ ; a vector, pointing along the direction of the so-called "invariable axis" of the atom. I designate it by  $P_A$ . The following equation shows the relation between the magnitudes of these three angular momenta and the angle  $\Theta$  between the two first-named, the angle which describes the relative orientation of the axes of rotation of the two flywheels:

$$P_A^2 = P_V^2 + P_R^2 + 2P_V P_R \cos \Theta \quad (6)$$

Remembering the successes which in dealing with the spectrum of hydrogen have resulted from assuming that the angular momentum of the entire atom is constrained to take only such values as are integer multiples  $Jh/2\pi$  of the quantity  $h/2\pi$ , we make the same assumption here. We further make the same assumption for each of the flywheels separately; the magnitudes of the angular momenta  $P_V$  and  $P_R$  are supposed to take only such values  $Vh/2\pi$  and  $Rh/2\pi$  as are integer multiples of the same quantity  $h/2\pi$ .<sup>5</sup> These particular assumptions, frankly, are foredoomed to failure; but the failure will be instructive.

Making all these assumptions together, we see that in effect we have laid constraints upon the angle  $\Theta$  which measures the relative orientation of the two flywheels. For if  $P_V$  is an integer multiple of  $h/2\pi$ , and  $P_R$  is an integer multiple of  $h/2\pi$ , then  $P_A$  which is fully determined by equation (6) cannot be an integer multiple of  $h/2\pi$  unless  $\Theta$  is very specially adjusted. To illustrate this by an instance (which will be clearer if the reader will work it out with arrows on a sheet of paper): if  $P_V$  and  $P_R$  are each equal to the fundamental quantity  $h/2\pi$ , and if  $P_A$  must itself be an integer multiple of  $h/2\pi$ : then  $\cos \Theta$  must take only the values,  $+1$ ,  $-\frac{1}{2}$ ,  $-1$ , which yield the

<sup>5</sup> All that is actually being assumed is, that  $P_V$  and  $P_R$  and  $P_A$  are all integer multiples of a common unit; nothing in this section will indicate either  $h/2\pi$  or any other value as the precise amount of that common unit.

values  $0, 2\pi/3, \pi$  for  $\theta$ , which yield the values  $2h/2\pi, h/2\pi, 0$  for  $P_A$ . Any other integer values for  $P_A/(h/2\pi)$  are unattainable by any value of  $\theta$  whatsoever; any value of  $\theta$  not among these three would yield a value for  $P_A$  not an integer multiple of  $h/2\pi$ , which is contrary to the assumptions. Thus, the assumptions that the atom is a conjunction of two whirling parts, and that the atom altogether and each of its two parts separately whirl with angular momenta which are constrained to be integer multiples of a common factor—these assumptions lead to the conclusion that the relative inclination of the two revolving parts is constrained to take one or another of a strictly limited set of values.

This essentially is the model devised by Landé to account for the complexity of the Stationary States. The several Stationary States which form a group belonging to a sequence—in other words, which share a common value of  $n$  and a common value of  $k$ , like the  $2p_1$  and  $2p_2$  states of sodium or the  $3d_1, 3d_2, 3d_3$  states of mercury—are supposed to resemble one another in this, that each of the whirling parts separately has the same angular momentum in every case; and to differ from one another in this, that in the several cases the two whirling parts are differently inclined to one another, so that the angular momentum of the entire atom differs from one state to the next. The different Stationary States which share common values of  $n$  and  $k$  are supposed to correspond to different orientations of the two parts of the atom and to different values of its angular momentum.

I will now no longer disguise the fact that these whirling parts are, or at any rate have been, supposed to be precisely the valence-electron and the residue. To the former we should therefore assign these values for the angular momentum  $P_V$ : the value  $h/2\pi$  for every state belonging to an  $s$ -sequence, the value  $2h/2\pi$  for every  $p$ -state,  $3h/2\pi$  for every  $d$ -state, and so on. Then to the angular momentum  $P_R$  of the residue we should assign a suitable constant value; a "suitable" value in this case being such a one, as would yield the proper grouping of terms in the various sequences of the system which the atom under consideration is known to have. Thus, for an atom-model to represent sodium with its doublet system we require a value for the angular momentum of the residue, such as will yield one permitted orientation when the atom is in an  $s$ -state ( $P_V = h/2\pi$ ), and two when it is in any state for which  $P_V = kh/2\pi$  and  $k$  is any integer greater than unity.

No such value can be found. The value  $P_R = h/2\pi$  will not do; for, as was shown in the illustrative instance a couple of pages back, it yields three permitted orientations when  $P_V = h/2\pi$ , and (as can easily be shown) three for each and every other value of  $P_V$  which

is an integer multiple of  $h/2\pi$ . Thus it would form an adequate model for a system of Stationary States in which every group of terms in every sequence was a triad; but this is not a doublet system, nor even a triplet system, nor any other observed system whatever. To make this long story short; it is impossible to simulate any of the eight groupings of terms set forth in the eight lines of Table I by assuming that  $P_V$ ,  $P_R$  and  $P_A$  are all integer multiples of  $h/2\pi$  (or of any other common factor).

It is in fact necessary to put  $P_V$  equal, not to  $h/2\pi$  and to  $2h/2\pi$  and to  $3h/2\pi$ , but to  $\frac{1}{2}(h/2\pi)$  and to  $\frac{3}{2}(h/2\pi)$  and to  $\frac{5}{2}(h/2\pi)$ , for the  $s$  and  $p$  and  $d$  states, respectively. This use of "half quantum numbers" makes it possible to produce an adequate model for an atom possessed of a doublet system, by assuming that the angular momentum  $P_R$  of its residue is always  $h/2\pi$ , and that its two whirling parts must always be so inclined to one another that the angular momentum of the entire atom is an integer multiple of  $h/2\pi$ .

For (to work out one example, and one only) when we make  $P_R = h/2\pi$  and  $P_V = \frac{1}{2}(h/2\pi)$ , then the greatest possible resultant that can be obtained by combining these vectorially is  $\frac{3}{2}(h/2\pi)$  and the least possible one is  $\frac{1}{2}(h/2\pi)$ ; these two extreme values being attained when the two component vectors are parallel and when they are anti-parallel,<sup>6</sup> respectively. If we permit for the resultant only such values as are integer multiples of  $h/2\pi$ , then there is only *one* that is permitted: the value  $h/2\pi$ —for this is the only such value lying within the possible range. Next, put  $P_R = h/2\pi$  and  $P_V = \frac{3}{2}(h/2\pi)$ . All possible values of the resultant lie between  $\frac{5}{2}(h/2\pi)$  and  $\frac{1}{2}(h/2\pi)$ ; within this range there are *two* of the integer multiples of  $h/2\pi$  which are the sole permitted ones. Next, put  $P_R = h/2\pi$  and  $P_V = \frac{5}{2}(h/2\pi)$ . All possible values of the resultant lie between  $\frac{7}{2}(h/2\pi)$  and  $\frac{3}{2}(h/2\pi)$ , and this range again includes *two* permitted values. Thus the model describes properly the grouping of the terms in a doublet system. I leave it to the reader to show that by putting  $P_R = 2h/2\pi$ , or  $3h/2\pi$ , or  $4h/2\pi$ , and treating  $P_V$  as in this foregoing case, he can reproduce the groupings of terms in quartet, or sextet, or octet systems, respectively, as Table I, describes them.<sup>7</sup>

A more drastic use of "half quantum numbers" is required to obtain an adequate model for atoms showing singlet and triplet and other

<sup>6</sup> This convenient word is used in German to describe vectors pointing in opposite senses along the same direction.

<sup>7</sup> The diagrams with arrows, offered by Sommerfeld in the fourth edition of his classic book, are very helpful in studying these models. Incidentally Sommerfeld's alternative way of arriving at the groupings of multiplet terms by compounding vectors is instructive.

systems of odd multiplicity. Thus to produce a singlet system it is necessary to put  $P_R = \frac{1}{2} (h/2\pi)$  always; to set  $P_V$  equal to  $\frac{1}{2} (h/2\pi)$  for all  $S$ -states, to  $\frac{3}{2} (h/2\pi)$  for all  $P$ -states, and so forth; and to suppose that the two whirling parts of the atom are constrained to take only such relative orientations as yield values for  $P_A$ , the angular momentum of the entire atom, which are odd integer multiples of  $\frac{1}{2} (h/2\pi)$ . It is easy to see that there is but one such orientation for an  $s$ -state, one for a  $p$ -state, and one for any other kind of state. To produce a triplet, or a quintet, or a septet system, it is necessary to put  $P_R = \frac{3}{2} (h/2\pi)$ , or  $\frac{5}{2} (h/2\pi)$ , or  $\frac{7}{2} (h/2\pi)$ , respectively; and to retain the just-stated assumptions about  $P_V$  and  $P_A$ .

The question whether these models have any intrinsic truthfulness has now become acute. If there is any doctrine in contemporary atomic theory which appears to be multiply tested and approved, it is surely the doctrine that the angular momentum of the valence-electron is always an integer multiple of  $h/2\pi$ . Yet in this passage I have spoken as if this principle had been indifferently and casually discarded, and replaced by a new principle to the effect that the angular momentum of the valence-electron is always an odd-integer multiple of  $\frac{1}{2} h/2\pi$ . It is hard to evade or mitigate this arrant contradiction.

A way out may possibly be found by suggesting that the partition of an atom into "residue" and "valence-electron," while appropriate when calculating energy-values by the method mentioned in Section P, is not appropriate in this instance; that the two whirling parts of the atom are respectively a system composed of a part of the residue, and a system composed of the rest of the residue and the valence-electron. This seems most admissible for such an atom as magnesium, consisting as it is supposed of what I have called a "kernel," and two additional electrons outside. The two whirling parts may be the kernel rotating as a unit, and the pair of outer electrons also rotating as a unit. It may be profitable to push the analysis even further, and to consider the two outer electrons each as an entity possessed of angular momentum, their two angular momenta combining with one another in such a fashion as I have lately described for the two parts of the atom; this resultant angular momentum of the two may then figure as the  $P_V$  employed in constructing the atom-model. There are decided possibilities in this way of thinking; but it is doubtful whether the difficulty about half-quantum-numbers can ever quite be removed.<sup>8</sup>

<sup>8</sup> An unfortunate feature of Landé's model in its original form is that it requires us to believe that the residue of each atom is different from the completed preceding atom. For instance since Mg has a singlet and a triplet system, its residue must have sometimes  $P_R = \frac{1}{2} (h/2\pi)$  and sometimes  $P_R = \frac{3}{2} h/2\pi$ ; whereas for the Na atom in its normal state  $P_A = h/2\pi$  by the theory.

It may be recalled from the First Part of this article that the different Stationary States of a group, sharing a common value of  $n$  and a common value of  $k$ , are distinguished from one another by having different values of a numeral which was designated by  $j$  and called the Inner Quantum-number. It was so chosen that the only transitions which occur are those in which  $j$  change by one unit, or not at all; while transitions between two states, in each of which  $j=0$ , are likewise missing. This numeral is correlated with the angular momentum  $P_A$  of the entire atom, in the theory here outlined. For systems of even multiplicity,  $P_A$  is equal to  $j\hbar/2\pi$ ; for systems of odd multiplicity,  $P_A$  is equal to  $(j+\frac{1}{2})\hbar/2\pi$ .

The various Stationary States of a group differ slightly in energy—otherwise, of course, they would never have been discerned. The energy-value of an atom must be conceived therefore as depending not merely upon  $n$  and  $k$ , not merely on the rates at which the two whirling parts are separately spinning, but likewise upon their mutual orientation and hence upon  $j$ . In this theory, the dependence of energy upon orientation must be postulated outright. We shall presently meet with a case in which the dependence of energy upon orientation can be foreseen, even in detail.

It appears from all these speculations, that a transition between two Stationary States is no longer to be conceived merely as a simple leap of an electron from one geometrically-definite orbit into another. A leap is indeed supposed to occur, but it is accompanied by a turning-inward or a turning-outward of the axes of rotation of the two spinning parts of the atom. The radiation which comes forth is a joint product of these two processes, in which however no features of either separately appear; only the net change in the energy of the atom, the algebraic sum of the energy-changes due to each process separately, is radiated as a single fused unit. Nature does not make the separation which our imaginations make.

#### T. MAGNETIC PROPERTIES OF ATOMS

Having used an orientation-theory to interpret the complexity of the Stationary States, we will now consider an orientation-theory developed to account for the effect of a magnetic field upon the Stationary States. There, it was supposed that the various States belonging to a single group are distinguished by various orientations of two spinning portions of an atom, relatively to one another. Here, it will be supposed that the various States which replace each individual State, when a magnetic field acts upon the atom, are distinguished



by various orientations of the spinning atom relatively to the field. It will presently be seen that the evidence for the orientation-theory is much more abundant and more nearly direct, in this case of magnetically-excited Stationary States, than in that former case of multiplets. This case in fact was the earliest to which an orientation-theory was applied; but for it, some quite different form of theory might have been developed for multiplets. Even here the data and the theory are not entirely concordant; but the concordance is so extensive, that the discord is sharply localized and identifiable.

From the Second Part of this article (Section L) I quote the principle that an electron (of mass  $\mu$ ) revolving in an orbit with angular momentum  $P$  is equivalent to a magnet of which the magnetic moment  $M$  is proportional to  $P$ , being

$$M = eP/2\mu c \quad (7)$$

Both  $P$  and  $M$  are vectors normal to the plane of the orbit and hence parallel to each other. If several electrons are revolving in divers plane orbits about the same nucleus, their separate angular momenta may be summed vectorially into a vector which is the angular momentum of the entire system, and their separate magnetic moments may likewise be summed vectorially into a vector which is the magnetic moment of the entire system; and these two summation-vectors will be parallel to one another, and related by the foregoing equation. Hence a rigidly-connected revolving framework of electrons—if such a thing there be—may be treated like a single electron, insofar as the ratio of magnetic moment to angular momentum is concerned. Wherever in the course of this article we have envisaged electrons, kernels, or atoms revolving with angular momenta prescribed as integer multiples of  $h/2\pi$  or of  $\frac{1}{2} h/2\pi$ , we might have imagined these as magnets with magnetic moments prescribed as integer multiples of  $eh/4\pi\mu c$  or of  $\frac{1}{2} eh/4\pi\mu c$ .<sup>9</sup> This is not necessary; though the relation between angular momentum and magnetic moment is derived directly from an equation valid for perceptible electric currents, it might not be true for individual electrons. Nevertheless we shall arrive at striking results, by supposing that it is.

When a magnetic field is applied to a multitude of radiating atoms, most of the lines of their spectrum are replaced by groups of several lines each, or “split up” into several components, as the phrase is. This signifies that each of the Stationary States of each atom is apparently replaced by several. One may infer that when an atom is

<sup>9</sup> The quantity  $eh/4\pi\mu c$ , the presumptive magnetic moment of an electron circulating in an orbit of angular momentum  $h/2\pi$ , is known as the *Bohr magneton*.

introduced into a magnetic field, each of its Stationary States is modified into one or another of several new States, differentiated from one another and from the original State to a small but appreciable extent. This might arise from some distortion or internal alteration of the atom by the field; and it will probably be necessary to adopt this view in some cases. But there is also a simpler effect which the magnetic field may have upon the apparent energy-values of the Stationary States, an effect not involving any deformation of the atom by the field—to wit, an orientation-effect similar to that which was assumed to account for multiplets. This we proceed to examine.

If an atom which is a magnet is floating in a magnetic field, it experiences a torque which tends to orient it parallel with the field. By saying that an atom is parallel or oblique to the field, I mean that the magnetic moment of the atom and therefore also its angular momentum, are directed parallel or obliquely to the field; and this usage will be maintained. Owing to this torque it is endowed with energy due to the field, in addition to its own intrinsic energy; this additional energy, which depends upon the inclination of the atom to the field, I shall call its *extra magnetic energy*. If the atom turns in the field, the amount of its extra magnetic energy changes; and if its magnetic moment suddenly changes, its extra magnetic energy also changes unless it simultaneously turns by just the right amount to compensate the change. If at the moment of passing over from one of its Stationary States to another, its inclination or its magnetic moment or both are changed; the amount of magnetic energy which it gains or loses will be added (or subtracted, as the case may be) to the amount of energy which it gains or loses because of the transition. The frequency of the radiation sent out or taken in by the atom will be equal to  $1/h$  times the sum of two energy-changes of distinct kinds—not, as in the absence of magnetic field, to  $1/h$  times the energy-difference between the two Stationary States alone. Thus the effect of a magnetic field upon spectrum lines might be ascribed, not to any deformation of the atom by the field, but to changes in the orientations or in the magnetic moments of the atoms occurring at the instants when they make their transitions. The question for us now is, whether the actual details of the observed effect can be interpreted in this manner.

Expressing the foregoing statements in formulae, in which  $M$  denotes the magnetic moment of an atom,  $H$  the magnetic field, and  $\alpha$  the inclination of the atom to the field, we have for the torque which the field exerts upon the atom

$$T = MH \sin \alpha \quad (8)$$

and for the "extra magnetic energy" of the atom due to the field

$$\Delta U = -MH \cos \alpha \quad (9)$$

In this last expression it is tacitly assumed that the extra magnetic energy is zero when the atom is oriented crosswise (at right angles) to the field. This is not an arbitrary, but a quite essential convention, justified from the atom-model.<sup>10</sup> Suppose now that the atom passes between two stationary states  $S'$  and  $S''$ , in which its internal energy, its magnetic moment and its inclination are denoted by  $U'$ ,  $M'$ ,  $\alpha'$  and  $U''$ ,  $M''$  and  $\alpha''$ , respectively. Were there no magnetic field, the frequency radiated would be

$$\nu_0 = (U'' - U')/h \quad (10)$$

but owing to the field, the frequency radiated is

$$\nu_H = \nu_0 + \Delta\nu = (U'' - U')/h + H (M' \cos \alpha' - M'' \cos \alpha'')/h \quad (11)$$

the term  $\Delta\nu$  representing the displacement of the line by the field. The question is, whether this term can be equated to the observed displacements.

Consider the most tractable cases, those in which the so-called "normal Zeeman effect" is observed. In these cases a line of frequency  $\nu_0$  is replaced by three, of which the frequencies are

$$\nu_0 + \omega H, \nu_0, \nu_0 - \omega H \quad (12)$$

corresponding to three values for the displacement  $\Delta\nu$ , which are expressed by

$$\Delta\nu = +\omega H, 0, -\omega H \quad (13)$$

The quantity  $\omega$  occurring in these expressions is a specific numerical constant. Comparing these with the expressions for  $\Delta\nu$  in (11), we see that if our model is to be used to interpret the observations, then for the first of the three observed lines  $M' \cos \alpha'$  must be greater than  $M'' \cos \alpha''$  by the amount  $h \omega$ ; for the second,  $M' \cos \alpha'$  must be equal to  $M'' \cos \alpha''$ ; for the third,  $M' \cos \alpha'$  must be less than  $M'' \cos \alpha''$  by the amount  $\omega h$ .

Another way of putting these statements is, that in order to interpret the normal Zeeman effect in this manner it must be supposed that whenever a transition occurs, the projection of the magnetic moment

<sup>10</sup> The action of the magnetic field upon the revolving electron imparts to it an extra angular velocity about the direction of the field (the Larmor precession) and hence an extra kinetic energy which (to first order of approximation) is proportional to  $-\cos \alpha$  and is zero when  $\alpha = \pi/2$ . This extra kinetic energy is the extra magnetic energy  $\Delta U$ . It is profitable to derive the entire theory in this manner.

upon the direction of the field—for this is precisely what  $M \cos \alpha$  is—either does not change at all or else changes by  $\pm \omega h$ . Sometimes it acts in the first of these ways, sometimes in the second, sometimes in the third; but never in any other.

This would result, if the behavior of the atom floating in the magnetic field were governed by two rules; *first*, that it may orient itself only in certain “permitted” directions such that  $M \cos \alpha$ , the projection of its magnetic moment upon the field-direction, assumes “permitted” values which are integer multiples of  $\omega h$ ; *second*, that whenever a transition occurs  $M \cos \alpha$  either retains the value which it had initially, or else passes to one or the other of the two adjacent permitted values.

The first of these rules is stated more rigorously than is quite necessary; all that is required is to say that  $M \cos \alpha$  is permitted to take only such values as belong to an equally-spaced series with intervals equal to  $\omega h$ . The second rule is necessary.

The theory of the normal Zeeman effect is simply, that the atom does behave according to these rules. Radiation of the frequency  $\nu_0$  occurs, either when the magnetic moment of the atom does not change and the atom does not turn, or when the magnetic moment changes and simultaneously the atom turns just so as to keep the projection of the magnetic moment on the field-direction constant. We shall later see that the latter of these two alternatives is the accepted one. It must be supposed that the atom, so to speak, capsizes when it emits the frequency  $\nu_0$  while floating in a magnetic field; it flops over at the same moment as it passes from one stationary state to another. Radiation of the frequency  $\nu_0 + \Delta\nu$  or of the frequency  $\nu_0 - \Delta\nu$  occurs, as we shall see, when the magnetic moment of the atom changes; in some cases the atom capsizes during the process, in others it does not.

I now translate the foregoing rules from the language of magnetic moments to the language of angular momenta. The first rule is, that the atom may orient itself only in certain permitted directions such that  $P \cos \alpha$ , the projection of the angular momentum upon the direction of the magnetic field, assumes permitted values which are consecutively spaced at intervals of  $(2\mu c/e)\omega h$ .

Now it is a fact of experience, that in the cases of the normal Zeeman effect,

$$\omega = e/4\pi\mu c. \quad (14)$$

The rule therefore reads, that *the projection of the angular momentum of the atom upon the direction of the magnetic field is constrained to take certain permitted values, spaced at intervals of  $h/2\pi$ .*

We have supposed, in dealing with multiplets, sometimes that the angular momentum of the entire atom is constrained to take such values as are integer values of  $h/2\pi$ , and sometimes that it is constrained to take such values as are odd-integer multiples of  $\frac{1}{2} (h/2\pi)$ .<sup>11</sup> In either case the permitted values of the angular momentum are spaced at equal intervals; and as the rule for the component of the angular momentum along the direction of the field bears the form which it does, we may well suppose that something in the order of nature constrains both the angular momentum and its projection to accept only values which form a sequence spaced always at that curious interval  $h/2\pi$ .

The total number of permitted orientations will obviously be limited by the actual magnitude  $P$  of the angular momentum. This being supposed always to be an integer multiple of  $\frac{1}{2} h/2\pi$ , let it be written  $P = 2J(\frac{1}{2} h/2\pi)$ . The permitted orientations are those which yield a series of values for the projection  $P \cos \alpha$  spaced at intervals  $h/2\pi$ ; let these be written

$$P \cos \alpha = A_0, A_0 - h/2\pi, A_0 - 2h/2\pi, \dots A_0 - mh/2\pi \quad (15)$$

Nothing in the experiments thus far described gives the least notion of the value which should be assigned to  $A_0$ . All we know at present is that  $A_0$  cannot exceed  $P$  and that  $(A_0 - mh/2\pi)$  cannot be algebraically less than  $-P$ . Suppose in the first place that  $A_0 = P$ ; that is to say, that the atom may orient itself with its axis parallel to the magnetic field. Then the permitted orientations are those which yield this series of values of the projection:

$$\begin{aligned} P \cos \alpha &= P, P - h/2\pi, P - 2h/2\pi, \dots P - mh/2\pi \\ &= 2J(\tfrac{1}{2} h/2\pi), (2J-1)(\tfrac{1}{2} h/2\pi), (2J-2)(\tfrac{1}{2} h/2\pi), \dots, 0 \end{aligned} \quad (16)$$

of which there are  $(2J+1)$  in all. On the other hand, it may be that the atom is prevented from orienting itself parallel to the field; that the least permitted angle between the axis of the atom and the direction of the field is some angle yielding a projection  $A_0$  intermediate between  $P$  and  $(P - h/2\pi)$ . Then there are  $2J$  permitted orientations altogether.

Summarizing the results of this last paragraph: if the angular momentum of the atom is an integer multiple  $2J(\frac{1}{2} h/2\pi)$  of the fundamental unit  $\frac{1}{2} (h/2\pi)$ , then according to the orientation theory

<sup>11</sup> It was remarked at the beginning of Section S that the evidence to be presented in that Section would support neither  $h/2\pi$  nor any other particular numerical value for the fundamental unit of angular momentum; here, however, we have evidence for that value.

the atom is permitted to take either  $(2J+1)$  or  $2J$  distinct orientations in the field; the former number if it is, the latter if it is not permitted to set itself quite parallel to the field.

It will now be shown that these are by no means idle speculations; they bear directly upon certain facts accessible to observation. Before bringing up these facts it is necessary to abandon the policy of speaking exclusively about the "normal" Zeeman effect. This "normal" effect received its adjective because it agrees so excellently with the original theory devised years before quanta were dreamt of to explain the effect of magnetic field upon spectra. It is essentially because of this agreement that it is possible to develop the contemporary theory of the "normal" effect in a perfectly deductive fashion, using no new assumptions beyond those general ones of the orientation-theory. Most spectrum lines, however, are affected by a magnetic field in ways not compatible with the original theory; which is a consequence of the fact that the set of new Stationary States, whereby a magnetic field supplants each original Stationary State, in most cases does not conform to the laws previously set forth.

The laws to which it generally does conform were read from the spectra by Landé. The one feature in which the foregoing theory quite agrees with these laws is its prediction of the total number of Stationary States. A Stationary State for which the angular momentum of the atom is determined, by virtue of the theory of multiplets which filled the preceding section of this article, as being  $2J(\frac{1}{2}h/2\pi)$ , is actually found to be supplanted, when a magnetic field is impressed upon the atom, by  $2J$  new Stationary States. This is in agreement with one of the two alternative predictions made a few paragraphs *supra*; to wit, with the prediction derived from the assumption that the atom cannot set itself quite parallel to the field. This agreement between the orientation-theory of multiplets and the orientation-theory of Zeeman effect considerably strengthens both.

The several Stationary States replacing a given original State are always equally spaced; but the spacing differs in amount from the value  $\omega Hh$  or  $eHh/4\pi\mu c$  exhibited when the normal Zeeman effect occurs, and which we found it possible to deduce from the simple orientation-theory. The difference is this, that the actual spacing is a multiple of the value  $\omega Hh$  by a factor  $g$  (generally lying between  $\frac{1}{2}$  and 2) which depends upon the original State:

$$\Delta U = g\omega Hh \quad (17)$$

The only ways hitherto used to accommodate the atom-model to this surprising and inconvenient factor  $g$  are tantamount to assuming that it enters into the relation between angular momentum  $M$  and magnetic moment  $P$  which was derived in Section I and written down here as equation (7); which relation is accordingly modified without discoverable reason into

$$M/P = g e/2 \mu c \quad (18)$$

a very unsatisfying procedure. Lande found it possible to mitigate this process somewhat and at the same time produce a partial explanation of the formula quoted in the First Part of this article, whereby  $g$  is related to the factors  $K$ ,  $R$  and  $J$  which, in the atom-model of the two whirling parts, measure the angular momenta of valence-electron and residue and entire atom respectively in terms of the common unit  $\hbar/2\pi$ . This explanation involved the postulate that  $g=1$  for the valence-electron and  $g=2$  for the residue. It would therefore be necessary to justify, or to postulate without justification, not a multitude of such relations as (16) with a multitude of unforeseen values of  $g$ , but only a single such relation with a single unforeseen value of  $g$ . This is bad enough, but not so bad as if it were inevitable to assume that  $M/P$  may have a dozen different values in different cases.

It is now the occasion to recur to the extraordinary experiments of Gerlach which disclose the magnetic moments of individual atoms and verify the supposition that certain orientations are permitted and others inhibited. These experiments having already twice been mentioned in this series of articles, I shall spend no more space upon the method than is necessary to say that atoms in a narrow stream are sent flying across an intense magnetic field with a strong field gradient, by which they are drawn aside. Were the atoms tiny magnets oriented randomwise in all directions, the beam would be broadened into a fan; one edge of the fan would be the path of atoms oriented parallel to the field, the other edge would be the trajectory of atoms oriented anti-parallel to the field, while the space between the edges would be filled by the orbits of atoms pointed obliquely to the field. Actually Gerlach observed not the whole fan, but two or several separate diverging pencils of atoms, and between them vacant regions traversed by none. Certain orientations of atoms to field were unrepresented in the beam. Here for the first time there is direct evidence of discrete Stationary States, of quantum permissions and quantum inhibitions, not deduced from observations upon transi-

tions but drawn forthright from viewing atoms in equilibrium in their Normal States.

When from the diverging pencils one proceeds to determine the orientations of the atoms and their magnetic moments, one is confused by a possibility made clear in the foregoing pages, but unsuspected at the time when the first of these experiments were performed. I illustrate with the case of silver, the atoms of which flock into two diverging pencils with a quite vacant space between. At first it was naturally supposed that one pencil consists of atoms oriented parallel, the other of atoms oriented anti-parallel to the field. The deflections of the two pencils are such, that if this assumption is true then the numerical value of the magnetic moment of the silver atom agrees within the error of experiment with the value of  $eh/4\pi\mu c$ —agrees, therefore, with the notions that the angular momentum of the silver atom in its normal state is  $\hbar/2\pi$  and that the magnetic moment stands in the right and proper ratio  $e/2\mu c$  to the angular momentum. The data were supposed to prove these notions. They also agree, however, with the suppositions that one pencil consists of atoms inclined at  $60^\circ$  to the field and the other of atoms inclined at  $120^\circ$ ; in which case the magnetic moment of the silver atom would be  $2eh/4\pi\mu c$ , suggesting that the ratio of magnetic moment to angular momentum has twice the right and proper value. This inextricable tangling of the effect of orientation with the effect of magnetic moment makes it impracticable to deduce quite so much from the data as was at first thought possible; but plenty still remains. It is found that copper and gold behave like silver, as was to be expected from their positions in the Periodic Table. It is found that lead atoms, and (most surprising of all!) *iron* atoms are not deflected at all; so that either the magnetic moments of their parts balance one another completely, or else they all orient themselves crosswise to the field. Nickel, on the other hand, behaves as though its atoms had each a magnetic moment surpassing  $2eh/4\pi\mu c$ , while thallium responds as though that of its atoms were much less than  $eh/4\pi\mu c$ . Finally—lest the results seem too gratifying—it is found that bismuth atoms are deflected in a manner quite unforeseeable.

There is not time nor space to speak of the other method for determining the magnetic moments of atoms, by measuring the susceptibilities of great quantities of them in gases or solutions; but the measurements so made are also very helpful in determining the magnetic moments of various atoms and ions—various groupings, that is to say, of electrons around nuclei.<sup>12</sup> All such data are of im-

<sup>12</sup> For the status of such measurements in 1923, the first of this series of articles may be consulted. (This Journal, September, 1923.)



mense value, and no theory of the atom can be spared from the demand that it confront them and account for them.

#### U. INTERPRETATION OF X-RAY SPECTRA

By the term "X-ray" the reader may understand any radiation of which the frequency  $\nu$  is so high, that the energy  $h\nu$  of a single quantum is several times as great as the energy required to remove the most-easily-detached electron from an atom; greater, for instance, than 100 equivalent volts, so that the wavelength of the radiation is less than some 125 Angstrom units. The emission or the absorption of such radiation by an atom involves too great an energy-change to be attributed merely to a displacement of the valence-electron or even to combined displacements of the valence-electron and one or two others. This definition leaves a sort of "twilight zone" of radiations having frequencies somewhat but not much greater than  $1/h$  times the ionizing-potential of an atom. Little is known about such radiations, and in this place they will not be considered.

The absorption of an X-ray quantum by an atom results in the extrusion of an electron from the atom. The emission of an X-ray quantum results from the passage of an electron within the residue of the atom from some original situation to the situation vacated by the extruded electron, or else into a situation vacated by an electron which itself has moved elsewhere within the atom. These statements contain the theory of the vast amount of data piled up by observations upon the emission and absorption of X-rays by matter.

To express the same statements rather differently: X-ray absorption-spectra and X-ray emission-spectra reveal, when analyzed for Stationary States in the manner used in analyzing optical spectra, that each atom with several or many electrons has a considerable number of Stationary States, distinguished from those we have heretofore discovered in that *each of them involves the absence of one electron from the atom*. Each of them is therefore strictly an "ionized-atom state," and yet there are several of them with extremely different energy-values. This signifies that the extraction of an electron from an atom rich in electrons may leave the residue in any one of several distinct conditions. These distinct conditions are the distinct Stationary States, transitions between which are responsible for X-ray spectra. Owing to this striking difference between the Stationary States hitherto described and these latter, I shall refer to these as the "X-ray Stationary States"—not that this name is a particularly good one.

Absorption of an X-ray quantum by an atom, then, results in a transition of the atom from its normal state to one of the "X-ray Stationary States." Emission of an X-ray quantum by an atom results from a transition of the atom from one into another of its "X-ray Stationary States"—a transition which begins in a condition in which the atom lacks one electron, and ends in another condition in which the atom lacks one electron. To take instances: radiation of an adequate frequency falling upon an atom in its normal state may put it over into an X-ray Stationary State known as the  $L_{II}$  state, an electron being extruded. Radiation of an adequate frequency (a higher frequency will be required) falling upon a similar atom in its normal state may put it over into another X-ray Stationary State of higher energy, known as the  $K$  state, an electron being extruded. The atom in the  $K$  state may then spontaneously pass over into the  $L_{II}$  state, emitting a radiation belonging to the X-ray emission-spectrum, its frequency being  $1/h$  times the energy-difference between the  $K$  state and the  $L_{II}$  state. Later the atom may pass into still another state, such as the  $M_I$  state, by emitting radiation of some frequency  $\nu'$ ; the energy of the  $M_I$  state is therefore less than that of the  $L_{II}$  state by the amount  $h\nu'$ ; calculating it thus, and then applying to normal atoms a stream of electrons or of quanta having energy just adequate to put them over into this  $M_I$  state, we find that this effect is duly produced.

Thus there is a thoroughgoing analogy between the genesis of optical spectra by transitions between the optical Stationary States, and the genesis of X-ray spectra by transitions between the X-ray Stationary States. The differences between the two kinds of spectra seem all to derive from the one fundamental difference between the two kinds of Stationary States; the former do not involve the absence of an electron from an atom, the latter do. In the optical region, for instance, we find that an atom in the normal state cannot be put into a particular excited state by any radiation except one of just the right frequency  $\nu_0$  for which  $h\nu_0$  is equal to the energy-difference between the normal state and the excited state in question. In the X-ray region, we find that an atom can be put into the  $K$ -state (for instance) by any radiation of frequency equal to or exceeding that critical frequency  $\nu_0$  for which  $h\nu_0$  is equal to the energy-difference between the normal state and the  $K$  state. This difference in behavior occurs because in the former case a quantum of radiation having frequency  $\nu$  exceeding  $\nu_0$  would have no place to put the left-over energy  $h(\nu - \nu_0)$ , whereas in the latter case this extra energy can be and is delivered over to the extracted electron as kinetic

energy, with which it flies away. This is known positively; for the extracted electrons can be observed, and their energy measured.

Spontaneous transitions from each of the X-ray Stationary States occur to some, but not to all, of the States of lesser energy. Some are evidently inhibited; and it is possible to lay down rules of selection, distinguishing those which are permitted. The complicated system of rules originally proposed has yielded place to a much simpler one, exactly similar to the one prevailing in the optical spectra. That is to say: it appears to be possible to assign to each of the X-ray Stationary States a certain value of a numeral  $k$  and a certain value of a numeral  $j$ , such that the only transitions which actually occur are those in which  $k$  changes by one unit and  $j$  either changes by one unit or does not change at all; while transitions between states in both of which  $j=0$  are specially excluded. Furthermore, the various values of  $k$  and  $j$  thus assigned to the several X-ray Stationary States are identical with those assigned to the several States constituting a doublet system, such as we have met already in Section S, such as the sodium atom possesses; so that there is a complete correspondence between the system of X-ray Stationary States which every atom rich in electrons possesses, and the doublet system of optical Stationary States which only certain atoms possess. A part of this correspondence is expressed in the following Table:

TABLE II

Values of $k$ :	1	1	2	2	1	2	2	3	3
Values of $j$ :	1	1	1	2	1	1	2	2	3
<i>Stationary States of</i>									
Doublet system:	1s	2s	2p <sub>1</sub>	2p <sub>2</sub>	3s	3p <sub>1</sub>	3p <sub>2</sub>	3d <sub>1</sub>	3d <sub>2</sub>
X-ray system:	K	L <sub>I</sub>	L <sub>II</sub>	L <sub>III</sub>	M <sub>I</sub>	M <sub>II</sub>	M <sub>III</sub>	M <sub>IV</sub>	M <sub>V</sub>

No doubt the implications of this close correspondence are deep; but just what they are is not yet obvious.

The fact that the residue, left behind when an electron is extracted from an atom, may exist in any one of several distinct States, is quite naturally interpreted as meaning that the various electrons of the complete atom are variously situated, or revolving in various distinct orbits; so that the several X-ray Stationary States differ essentially in this, that differently-located electrons have been removed, leaving different places untenanted. This notion is easily combined with the idea that an atom is formed, or at all events behaves as though it had been formed, by successive self-annexations of electrons to a nucleus originally bare. Suppose that an atom is made by con-

secutive adhesions of electrons, each of which settles down into a peculiar orbit and remains there more or less unperturbed as the later comers immigrate one after the other into the system. May not then the process of X-ray absorption consist in a powerful intruding entity, electron or quantum, violently invading the interior regions of the atom and casting out one or another of the deeper-lying earlier-added electrons, while the later-added ones nearer or upon the frontier remain attached? May not X-ray emission consist in the passage of one of these latter electrons into the orbit formerly held by its predecessor, now unexpectedly reft away and its place left empty?

Although an affirmative answer to these questions involves a very literal and concrete conception of electron-orbits, most physicists make it, and would like to prove it. The chief difficulty lies in the fact that all information about X-ray Stationary States is primarily information, not about the prior condition of the electron which is gone, but about the final condition of the residue which is left behind.

The data show at all events that there are not nearly so many conditions of the residue, as there are electrons of the completed atom; from which it is fairly safe to conclude that the electrons of the atom are so arranged, that any one of several different electrons may be removed and the residue be left always in the same condition—therefore, that the electrons are arranged in groups, each electron being situated essentially like every other of its group. In discussing the formation of an atom by successive binding of electrons, it was remarked that several electrons may be bound in orbits each characterized by a common value of  $n$  and a common value of  $k$ . These two ideas may coincide; and great efforts are being made to bring them into entire coincidence. The evidence indicates, for example, that the first ten electrons bound to a nucleus are divided into four groups. Absence of an electron from one of these groups entails that the atom is in the  $K$  state; absence of an electron from the second, third, or fourth group brings it about that the atom is in the  $L_I$ , or  $L_{II}$ , or  $L_{III}$  state, respectively. So much the X-ray data do show rather definitely; although the actual number of electrons in each of the four groups cannot yet be deduced. If one could prove *a priori* that the first ten electrons annexed by a nucleus settle down into orbits of four distinct kinds, the achievement would be a great one. Intimations that something of this sort has been achieved are made every now and then; but it is difficult to tell whether the assertions which are made have been derived cogently from a principle or are inspired guesswork.

There is a remarkable numerical agreement in this field, the meaning

of which was until a couple of years ago regarded as perfectly distinct; but at this moment it is beclouded by one of the curious contradictions so abundant in the Theory of Atomic Structure. Briefly, the typical phenomenon is this: the differences between the energy-values of the  $K$ ,  $L_{II}$  and  $L_{III}$  states agree notably well with what would be expected *if* the complete atom contains a few electrons moving in  $1_1$  orbits, a few in  $2_1$  orbits and a few in  $2_2$  orbits about the nucleus; and *if* the  $K$  state corresponds to absence of an electron of the first group, the  $L_{II}$  state to absence of one out of the second and the  $L_{III}$  state to absence of one out of the third. (The reason why calculations can be made for so indefinitely-phrased a model is this, that the field due to the highly charged nucleus of a massive atom should dominate over those of the individual electrons so that it does not make very much difference how many are supposed to be in each group.) The natural inference is, that the rest of the atom remains unchanged or little changed when any one of these electrons is extracted. In this case the Azimuthal Quantum-number of the residue should differ by one unit for the two states  $L_{II}$  and  $L_{III}$ . Consulting Table II, one finds that the quantity called  $k$ , which obeys the characteristic selection rule of the Azimuthal Quantum-number, is the same for  $L_{II}$  as for  $L_{III}$ . This is an illustration of the collisions between two sets of inferences which unsettle the supposedly firmest achievements of this theory.

Of the *theory of molecules*, a subject large enough for an article by itself, I can say here nothing more than that it attains some remarkable successes, achieved by and therefore fortifying some of the assumptions made in these pages; notably the assumption that Angular Momentum is a thing required in Nature to assume discrete values spaced at intervals of  $h/2\pi$ .

The final part of this long article has been very unlike the Second Part, in which an atom-model for the atoms of hydrogen and ionized-helium was constructed and endowed with certain fundamental qualities, so that it reproduced almost all of the relations of these atoms to radiation with a truly striking fidelity. This Third Part by contrast has been a thing of shreds and patches. Models for many atoms have been brought forth, but they have not been thoroughly adequate and they have not been concordant with one another. Some were designed with the same fundamental qualities as those given to the model for hydrogen; and scarcely more can be said for any of them, than that it does not positively clash with the properties of the element for which it is devised. Others were made competent to deal with a

certain limited set of facts (as the grouping of terms in multiplets) by giving them qualities gravely in discord with those attributed to the atom-model for hydrogen; and then they proved themselves surprisingly well able to account for isolated facts of quite a different sort (as the effect of magnetic fields upon atoms). The presentation in these pages is naturally very far from complete; had it been complete, it would have filled a book and not an article. But if it had been complete, the eventual impression would have been the same; an impression of confusion, yet of a confusion full of hope.

For the "Theory of Atomic Structure" is distinguished especially by this, that it is not one theory but a multitude of partial theories, each designed and competent to cover a limited family of the abounding data, each struggling to overlap and to absorb the others. It may be compared with a cross word-puzzle or a map-puzzle, in which the beginnings of a solution have been made in half-a-dozen corners and patches, while wide blank areas adjoin and separate them, and some of the partial solutions already entered upon the field may finally yield to others which can be unified into the perfected pattern. Or it may be compared with those maps of polar regions, in which here and there a properly-surveyed island or little strip of coastline emerges from the blankness of the unexplored realms, and some of them are certainly misplaced relatively to the others and will be shifted on the map when all the geography is at length made known. Or it may be compared with the state of a congealing metal, in which a multitude of little crystals have formed themselves about casual nuclei of crystallization; each is oriented in a different way, and when two of them grow into contact with one another they clash and cannot merge, they stand blocking and thwarting one another. It may be necessary to reliquefy them all and make a new attempt to change the formless mass into a single crystal.

Meanwhile the work is driven forward with the fervor of discovery and exploration, in this period which Russell finely called the "Heroic Age of Spectroscopy," and not of spectroscopy alone. Many, though not so many as are needed, are busy with determining the Stationary States by deciphering the rich and cryptic spectra of some among the numerous unstudied elements—enormously numerous, taking into account how many kinds of ionized atoms there are; and others with the assembling of new photographs of spectra made under the most varied sorts of excitation, with other aids to discriminating the lines; and others with the impressing of electric and magnetic fields upon radiating atoms; and others are engaged in measuring the intensities of lines. Yet other experimenters are determining the magnetic

moments of various atoms in all the possible ways. Some are seeking new phenomena which may result from Stationary States and from transitions, and occasionally they are rewarded with brilliant examples such as that vivid demonstration of the atom-magnets which Gerlach effected, or such as the passage of an atom from one State to another while it transfers the liberated energy to another particle directly and produces a chemical change. Others are finding the processes resulting from the Stationary States manifest on an unearthly scale within the stars.

The theorists likewise are at work with furious industry. Now and then a set of data hitherto rebellious is suddenly systematized, usually in a manner not quite concordant with the other theories holding other parts of the field. Attempts are made to unify one partial theory with another, usually unsuccessful. Sometimes an authoritative thinker, despondent over the continuing contradictions, tries to cut all the knots by declaring that one or another of the conflicting models is entirely fallacious, and that the numerical agreements on which it is founded are a delusion and a snare. Another is driven to concede that the conflicts are destined to endure forever, and accepts all of the partial theories as equally valid, or else paraphrases them in ingenious words which veil the contradictions, yet leaving these essentially unabated. Others, abandoning the general problem, have returned to the question of the hydrogen atom, and for this they are trying to rephrase or reshape the Quantum Conditions in a manner more satisfactory to themselves; sometimes with the aid of new and unfamiliar forms of mathematics, apparently expecting that when these become habitual to the human mind, the mystery of the Quantum Conditions will seem simple and clear. That, of course, always remains a possibility—that the human intellect will accustom itself so thoroughly to the new systems of ideas that they will cease to seem incoherent, as the human ear has so accustomed itself to the harmonic innovations of successive generations of musicians that the tones which seemed outrageous discords to the audiences of Beethoven now are to us monotonously sweet. To our minds the various divisions of the Atomic Theory are still discordant. It would not be fair to leave any other impression of this strange and fascinating theory; inchoate but full of promise, immature but gathering force, a fantastic assemblage of failures and successes; irreconcilable with all other theories, irreconcilable even with itself, and yet perhaps predestined to refashion all the science of physics in its own image.